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METHODS OF IRON ANALYSIS

BY
FRANCIS C. PHILLIPS

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METHODS FOR THE ANALYSIS

—OF—

Ores, Pig Iron and Steel

IN USE AT THE

Laboratories of Iron and Steel Works

—IN THE—

REGION ABOUT PITTSBURG, PA.

TOGETHER WITH AN APPENDIX CONTAINING VARIOUS SPECIAL METHODS OF ANALYSIS OF ORES AND FURNACE PRODUCTS.

Contributed by the Chemists in Charge, and Edited by Francis C. Phillips.

SECOND EDITION.

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Preface to the First Edition.

These methods, in use in the iron and steel laboratories of the region near Pittsburg, Pa., were collected and published by the Engineers' Society of Western Pennsylvania during 1896. The supply of copies having been exhausted, in response to a continuous demand, the publication in more convenient form has been undertaken by The Chemical Publishing Company who have been authorized to do so by resolution of the Society at a meeting held March 13, 1897. These methods were detailed by the chemists in response to the following circular sent out by the committee in charge:

CHEMICAL SECTION—ENGINEERS' SOCIETY OF WESTERN PENNSYLVANIA, PITTSBURG, PA.

In accordance with a resolution of the Chemical Section of the Engineers' Society of Western Pennsylvania, the undersigned wish to ask your cooperation in an effort to collect for publication in the proceedings of the society the methods of analysis in use in the various iron and steel works laboratories of the region.

In calling the attention of chemists to the plan and asking their aid in its fulfilment, it should be mentioned that it is the aim of the section to secure accurate statements of analytical processes, describing with minuteness and clearness the successive steps, in order that the proposed compilation may represent as correctly as possible the present status of analytical chemistry as applied to iron and steel.

A full presentation of the methods in general use is likely to prove of interest and value, but the completeness and promptness of the responses received from a large number of chemists must determine the success of the measure.

In case you are willing to cooperate, you are requested to send to any one of the undersigned a full description of the methods you use for the determination of the following substances:

In Ores—Silica, iron, phosphorus, manganese.

In Pig Iron—Silicon, sulphur, phosphorus, manganese.

In Steel—Carbon (by combustion), sulphur, phosphorus, manganese, nickel.

SUGGESTIONS.

1. If the method is described in a text-book or journal, a mere reference will suffice, but any deviations from the published methods should be noted.

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2. In writing a description of a method it is very desirable that minute details should be given (*e. g.*, weights taken, volume of solution, temperatures, etc., etc.).

3. If more than one method is used, please describe the one in every-day use on which the commercial transactions of the firm are based.

4. It is earnestly requested that a reply be sent at the earliest possible date.

Each method will be published over the name of the sender. The work of the committee will be confined to collecting and arranging for publication without comment or discussion.

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A. G. MCKENNA,
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E. S. JOHNSON,
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Committee.

Preface to the Second Edition

In modern iron and steel works practice it has become a matter of importance that the chemical composition of all raw materials and of the products of manufacture should be accurately ascertained. Not only is this required, but the demand is constantly made for greater rapidity in the analytical processes, in order that the proportion of the various constituents of the products may be known, as far as possible, at the completion of each stage in a series of metallurgical processes. Steel works chemists are constantly striving to shorten the course of analytical procedure without sacrificing accuracy of results, and it may be said that with the great saving of time effected by the changes in methods of analysis during recent times greater accuracy is secured than was possible by the older and slower methods.

Considered as a whole the methods described in this second edition of the work are more rapid than those of the earlier edition, and they insure a greater degree of accuracy. In editing, care has been taken to present the methods in such manner as to reproduce the exact meaning of the authors.

FRANCIS C. PHILLIPS.

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I. Methods Used at the Laboratory of the Carnegie Steel Company, Edgar Thomson Steel Works, Furnaces and Foundry, Braddock, Pa.

By C. B. Murray

Determination of Silica in Iron Ores

One gram of ore, dried at 100° C., is weighed into a 350 cc. beaker, 50 cc. strong hydrochloric acid are added, and the mixture boiled till decomposition is complete. Dilute with water and filter. The residue is fused in a platinum crucible with sodium carbonate. The fusion is dissolved out in the original solution, which is then evaporated to dryness, and the residue heated till acid fumes can no longer be detected. The residue is moistened with hydrochloric acid, diluted with water, the solution boiled and filtered. Wash thoroughly with hot water and dilute hydrochloric acid. Ignite and weigh as SiO_2.

Determination of Iron in Ores

One-half gram of the ore is dissolved in 50 cc. of hydrochloric acid. In case the residue left is not white the solution is filtered, the residue fused with sodium carbonate, dissolved in hydrochloric acid, the iron precipitated as hydroxide, dissolved in dilute hydrochloric acid, (1:1) and the solution added to the main solution. As a rule there is no iron left in the residue, and then a fusion is unnecessary.

To the hot solution of the ore, stannous chloride solution is added from a burette, drop by drop, stirring constantly until the solution is colorless. Three drops in excess are then added. After allowing a few minutes for the stannous chloride to complete the reduction of any ferric chloride adhering to the silica, dilute to about 400 cc. with cold water, add *all at once* 20 cc. mercuric chloride solution and stir vigorously. Now titrate with a

standard solution of potassium dichromate, adding an amount of the solution sufficient to nearly oxidize all the iron. Place on a white tile several drops of potassium ferricyanide solution. Take out a drop of the solution in a beaker and let it fall into a drop of the ferricyanide solution. Continue adding dichromate and testing as described until the blue color is faint. Then take two drops for every test. Wait one-half minute at every test for the color to develop. When no blue color appears at the end of one-half minute take the burette reading which gives directly the percentage of iron in the ore.

SOLUTIONS

The Potassium Dichromate Solution contains 4.4 grams of the salt in 1 liter of water. 1 cc. corresponds to 0.005 gram iron, or to 1 per cent. when 0.5 gram of the ore is employed.

The Mercuric Chloride Solution contains 50 grams of the salt in 1 liter.

The Stannous Chloride Solution contains 50 grams in 1 liter.

The Potassium Ferricyanide Solution contains two or three pieces of the size of pin heads in 50 cc. of water. This solution is prepared every other day.

Determination of Phosphorus in Ores

Two grams of the dried ore, or 3 grams if the phosphorus is known to be very low, are weighed into a 350 cc. beaker, 50 cc. strong hydrochloric acid are added and the solution boiled, until the ore is apparently decomposed. Filter, using suction. Fuse the residue with sodium carbonate. Dissolve in hydrochloric acid (1:1) and evaporate both the main solution and the solution of the fusion to dryness separately. When dry, moisten each with 10 cc. hydrochloric acid and dilute with water. Heat until dissolved and then add 20 cc. nitric acid to each. Evaporate until all the hydrochloric acid is driven off. Filter both solutions through the same filter, into a 500 cc. Erlenmeyer flask. To the combined filtered solutions, add 25 cc. ammonia, and then enough nitric acid to dissolve the iron hydroxide and bring the solution to a rich amber color. Bring the solution to a temperature of 50° C., and pour in 60 cc. ammonium molybdate solution, and shake for five minutes. Allow to stand for half an hour, or until

the precipitate has settled, leaving a clear solution. Filter through a 9 cm. weighed filter-paper, wash with 2 per cent. nitric acid solution, dry for an hour at 100° C., and weigh. 1.63 per cent. of the weight is phosphorus.

SOLUTIONS

Molybdate Solution.—Dissolve 150 grams molybdic acid in a mixture of 267 cc. ammonium hydroxide (sp. gr. 0.90) and 400 cc. water. Pour this solution into 1667 cc. nitric acid (sp. gr. 1.20) and allow to stand in a warm place over night. Filter and it is ready for use.

Determination of Manganese in Ores

Dissolve 1 gram of the ore dried at 100° C. in 25 cc. strong hydrochloric acid. When all is in solution dilute with an equal bulk of water and filter. Wash twice with hot water, ignite the residue till the filter-paper is destroyed, cool, add to the contents of the crucible 2 or 3 drops of sulphuric acid and a little hydrofluoric acid, evaporate to dryness to expel the silica, fuse the residue with about 3 grams of sodium carbonate, dissolve the fusion in the original filtrate from the first solution, and evaporate this to dryness in the sand-bath. Take up with 150 cc. of strong nitric acid, boil for about twenty minutes, and then add 5 to 8 grams of potassium chlorate, a little at a time. When enough has been added to oxidize all the manganese the solution will produce a slight puff. Now add 1 gram more of potassium chlorate and boil the solution for two minutes. Cool and filter through a prepared asbestos filter or plug; wash the beaker and plug twice with strong nitric acid. The filtrate should then be boiled and more potassium chlorate added to ascertain whether all the manganese has been precipitated. The manganese dioxide on the asbestos plug, together with the plug, is now returned into the same beaker in which the precipitation was made. Dissolve in 25 cc. of hydrochloric acid and boil for a few minutes. The asbestos is filtered off and a few drops of sulphuric acid are added to precipitate barium, which is generally found in manganese ores. Allow to stand about two hours. Now add ammonia until a faint precipitate appears, then 25 cc. of ammonium acetate solution. Boil for one minute. remove from the heat, and, as soon as the precipi-

tate has subsided, filter. Wash three times with hot water. Dissolve the precipitate on the filter in hydrochloric acid (1:1), and allow to flow into the beaker in which the first basic acetate separation was made. Make a second basic acetate separation in the same manner as before, combine the filtrates and dilute to about 400 cc. Add 40 cc. of ammonium phosphate solution, acidulate with hydrochloric acid, boil, and add ammonia, drop by drop, with constant stirring, until all the manganese is precipitated, and the precipitate has assumed a crystalline appearance. Allow the solution to cool, filter (using suction), wash three times with hot water, ignite and weigh as $Mn_2P_2O_7$.

SOLUTIONS EMPLOYED

Ammonium Acetate Solution.—Dissolve 450 grams of the salt in 8 liters of water.

Ammonium Phosphate Solution.—Dissolve 560 grams of the salt in 2.5 liters of water.

Determination of Manganese in Manganiferous Iron Ores

Dissolve 1 gram of iron ore in 50 cc. hydrochoric acid. Evaporate to dryness on the steam-bath. Take up in 20 cc. nitric acid and evaporate to about 10 cc. Wash into a 500 cc. flask, dilute to about 200 cc., and add zinc oxide stirred up in water until the iron is all precipitated. Dilute to 500 cc., make acid, shake well, allow the precipitate to subside and decant 250 cc. into a flask. Boil for about five minutes. Titrate with a standard solution of potassium permanganate.

Determination of Silicon in Pig Iron

Dissolve 1 gram of iron in 20 cc. of strong hydrochloric acid in a platinum dish. Evaporate to dryness over a bare flame. Heat for one minute after the residue is dry. Remove from the heat and add 10 cc. hydrochloric acid and about 25 cc. water. Boil, filter, ignite and weigh as SiO_2.

Determination of Sulphur in Pig Iron

Dissolve 5 grams of drillings in 100 cc. hydrochloric acid (1:1) in a 500 cc. flask. The flask is provided with a doubly perforated rubber stopper, carrying a funnel tube reaching to the bottom of the flask, and a delivery tube, for leading the gas down into a

25 x 2.5 cm. test-tube. Into the test-tube pour 50 cc. potash solution. As soon as the acid is added the flask is placed over a low flame with the delivery tube reaching to the bottom of the test-tube. After the gas has nearly ceased to come off, the heat is increased and the solution boiled until the delivery tube is hot as far as the test-tube. Remove the test-tube and wash out into a white dish. Dilute to about 500 cc. with water, and titrate with standard iodine solution, using starch solution as an indicator.

SOLUTIONS USED

Caustic Potash Solution.—Dissolve 1 pound in 17 liters of water.

Starch Solution.—Dissolve 4 grams starch in a liter of boiling water, cool and decant off the clear liquid for use.

Iodine Solution.—Dissolve 13 grams iodine and 18 grams potassium iodide in 2100 cc. water. This is the "stock" solution. Of this solution 1050 cc. are diluted to 10 liters and used for the titrations. The solution is standardized by a standard steel and a standard "shot" sample, in both of which the sulphur has been accurately determined.

Determination of Phosphorus in Pig Iron

Dissolve 1.63 grams of iron in 25 cc. nitric acid (sp. gr. 1.20) in an 11 cm. porcelain dish. Evaporate to dryness over a flame and bake for a half-hour. Take up in 20 cc. hydrochloric acid and evaporate to about 4 cc. Add about 5 cc. nitric acid and heat until red fumes cease to appear. Dilute and filter into a 250 cc. Erlenmeyer flask. Add ammonia until the iron is all precipitated, then nitric acid until all is redissolved and the solution is of an amber color. Heat to 40° C. and add 50 cc. molybdate solution.

Shake for five minutes and allow to stand for half an hour. Filter and wash with 2 per cent. nitric acid and twice with strong alcohol. The filters are then placed in a water-bath and heated for one hour. They are then placed between watch-glasses and weighed in "clips". The filters are dried for the same length of time and weighed before they are used for the filtration of the yellow precipitate. Since 1.63 grams of iron were used (calling the percentage of phosphorus in the yellow precipitate 1.63) every milligram represents 0.001 per cent. phosphorus.

The solutions used are the same as in the case of the determination of phosphorus in ores.

Determination of Manganese in Pig Iron

One gram of iron is dissolved in 25 cc. nitric acid (sp. gr. 1.20), Evaporate to about 10 cc. and proceed as in the case of manganese in manganiferous iron ores.

Determination of Carbon in Steel

Two grams of the steel are digested with 100 cc. of the copper and potassium chloride solution. After all is in solution but the precipitated copper, filter into a platinum boat or an asbestos felt. Wash five or six times with dilute hydrochloric acid (1:1) and hot water. Remove the boat from the filter and dry. For the combustion a platinum tube is used, containing in the rear end 15 cm. of coarse copper oxide, held in place by platinum gauze plugs. The oxygen used in the combustion is purified by passing first through a bottle of potash solution, then through a jar of solid potash. A 10-burner Bunsen furnace is used. After introducing the boat into the tube and starting the oxygen, four burners are lighted under the copper oxide. When this part is red hot, all the burners are lighted and the oxygen passed through the tube for ten minutes longer. The carbon dioxide is received in a barium hydroxide solution, contained in a modified Meyer tube, containing six bulbs. About 50 cc. of the barium hydroxide solution are sufficient. At the end of ten minutes, the oxygen is shut off and air passed through the same train for ten minutes. No purifying train is used between the platinum tube and the Meyer bulb-tube. The bulb containing the barium carbonate is detached and the solution filtered as rapidly as possible, using suction, through a 9 cm. filter-paper. The bulb is easily washed clean. The filter-paper with the barium carbonate is placed in a platinum crucible, which is heated gently until the paper is burned, and then placed in the muffle furnace and heated till the contents are white.

Weigh as $BaCO_3$, of which 6.09 per cent. are carbon.

SOLUTIONS

Cupric Potassium Chloride Solution.—2250 grams of the double salt are dissolved in 6.5 liters of water and the solution filtered through asbestos. Ammonia water is then added until a slight permanent precipitate appears. As the solution is used it is made acid by adding 5 per cent. of hydrochloric acid.

Barium Hydroxide Solution.—Twenty-five grams of barium hydroxde are dissolved in 1 liter of water.

Determination of Sulphur in Steel

The method is the same as in the case of sulphur in pig, 5 grams being used, however.

Determination of Phosphorus in Steel

Dissolve 1.63 grams of steel in 25 cc. nitric acid (sp. gr. 1.20) and proceed in the same manner as in the case of pig iron except that the filtration for the removal of graphite is unnecessary.

Determination of Manganese in Steel

Dissolve 1 gram of steel in 25 cc. of nitric acid (sp. gr. 1.20) and proceed as in the case of pig iron.

Determination of Nickel in Steel

Dissolve 1 gram of drillings in a 250 cc. Erlenmeyer flask, in 30 cc. hydrochloric acid (sp. gr. 1.10). Boil until all is in solution, then add 3 cc. nitric acid (sp. gr. 1.20) to oxidize the iron. Evaporate the solution to 10 or 15 cc. Cool and pour into a separatory funnel, washing out the flask with hydrochloric acid (sp. gr. 1.10), keeping the bulk of the solution as small as possible. Pour into the funnel 50 cc. ether, insert the stopper and shake violently for from five to eight minutes. Allow to stand until the ether solution of the ferric chloride has separated and risen to the top, leaving the aqueous solution of the other chlorides, nickel, copper, aluminum, at the bottom. Run the lower solution out into a beaker, or into another separatory funnel, and repeat the treatment with ether. Again draw off the lower solution into a beaker and boil until all the ether has been expelled. Make the solution ammoniacal, precipitating any iron which may be left, filter and wash thoroughly. Dissolve the iron from the filter-paper with dilute hydrochloric acid (1:1), and repeat the precipitation. Filter and combine the two filtrates. Neutralize the combined filtrates with acetic acid, then make *just* ammoniacal to litmus paper and pass hydrogen sulphide gas into the solution for fifteen minutes. Make the solution acid with acetic acid, using litmus paper as an indicator, and boil until the precipitated sulphide of nickel settles. Filter, ignite, and weigh as nickel oxide,

of which 78.58 per cent. is nickel. If copper be present in the steel it will be weighed with the nickel oxide. To purify the nickel oxide dissolve in hydrochloric acid, dilute, and pass hydrogen sulphide gas through the solution, which will precipitate out the copper. Filter, make the filtrate ammoniacal, pass hydrogen sulphide into the solution for fifteen minutes, make acid with acetic acid and boil. Ignite and weigh as pure nickel oxide.

II. Methods Used at the Laboratory of the Ohio Steel Company, Youngstown, Ohio.

By J. C. Barrett

Determination of Silica in Ores

Weigh 5 grams of ore which has been dried at 100° C., dissolve in 75 cc. strong hydrochloric acid, evaporate to dryness, add 30 cc. strong hydrochloric acid, and when dissolved dilute and filter, washing with dilute hydrochloric acid and water. The residue is then burned and fused. The fusion is dissolved in water, made acid with hydrochloric acid, and evaporated to dryness. Take up with hydrochloric acid and water, filter, and wash well with water. Put into a crucible wet, heat gently until all is dry and the paper has become well charred; then heat in a muffle until white, and weigh.

Observe precautions for TiO_2 and $BaSO_4$.

Determination of Iron in Iron Ores

The ore is well ground, dried at 100° C. for one hour and cooled in a desiccator. Weigh quickly 1 gram and brush into a small beaker. Add from 2 to 6 cc. of stannous chloride solution, according to the percentage of iron present, and 10 to 15 cc. of strong hydrochloric acid. Place over a lamp and boil for a few minutes, when the iron is soon dissolved and mostly in the ferrous condition. The ore being finely ground shortens the time for solution. The iron is completely reduced now by adding (a drop at a time) stannous chloride solution from a burette, continually agitating the solution in the beaker by a rotating motion, and using care not to add any after the solution is colorless. Five cc. of a saturated solution of mercuric chloride are then added to take up the slight excess of stannous chloride. Now pour the solution at once into a No. 5 beaker, in which 10 cc. of titrating solution have been placed. Dilute with water until the beaker is two-thirds full, and titrate with a standard solution of potassium permanganate. The stannous chloride solution is made by dissolv-

ing 1 pound of stannous chloride in 1 pound of concentrated hydrochloric acid and diluting to 2 liters. The "titrating solution" is made by dissolving 160 grams of manganous sulphate in water and diluting to 1750 cc., and adding 330 cc. of phosphoric acid and 320 cc. of sulphuric acid. The potassium permanganate solution is made by dissolving 22.9 grams in water and diluting to 4 liters. One cc. is equal to 1 per cent. of iron. Standardize with a known quantity of pure iron. This method is given by Mixer and DuBois.

The following method is also used for the determination of iron in iron ores.

The ore is dried at 100° for one hour and cooled in an exsiccator. Weigh quickly five grams of the ore, dissolve in a dish with 75 cc. concentrated hydrochloric acid, and evaporate to dryness on a sand-bath. Redissolve in 30 cc. strong hydrochloric acid, and when all is in solution evaporate to a very small bulk. Dilute with hot water, filter, washing with as little dilute hydrochloric acid as possible. Wash well with hot water. Burn the silicious residue and, if colored by iron, fuse. Dissolve and make acid with hydrochloric acid and evaporate to dryness to separate the silica. Take up with as little hydrochloric acid as possible and filter into the main solution, which should be in a graduated 500 cc. flask, which has been calibrated accurately with a 100 cc. pipette. Keep at the temperature of the room and fill with water of the same temperature to the mark, mixing well. Take 100 cc. with the same pipette with which you have checked the flask and bring into a flask of 500 cc. capacity, fitted with a rubber stopper having a Bunsen valve. Add 100 cc. of sulphuric acid (1:4), and then 15 grams of zinc. Keep cool for a time, then add 10 grams more of zinc if necessary. When all action is over heat moderately, but not to boiling. Cool, pour into a No. 5 beaker into which 50 cc. of sulphuric acid (1:4) have been poured. Wash out the flask well, decanting from the residue from the zinc; fill the beaker to a little more than half full, and titrate with standard solution of potassium permanganate, making allowance for a blank on the zinc which is carried along side by side with the ore, using the same weight of zinc in the blank as for the ore. In

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presence of titanium reduce with hydrogen sulphide. Remove the hydrogen sulphide and titrate.

Determination of Phosphorus in Ores

Dissolve 5 grams of ore ground and dried at 100° C. in a dish in about 50 cc. of concentrated hydrochloric acid. Boil over a lamp for about one-half hour. Remove, dilute, and filter into another dish. Place the insoluble residue in a crucible, burn off the paper and fuse with sodium carbonate. Remove from the crucible by putting a platinum rod into the fusion and allowing to cool, then add water and warm over a lamp and the whole is removed. Place the fused cake, still attached to the platinum rod, in the original dish, dissolve from the rod with water, and acidulate with hydrochloric acid. Wash out the crucible with hydrochloric acid and add to the dish. Evaporate both solutions to dryness. Take up the evaporated residue in the dish with the iron solution, add 40 cc. of hydrochloric acid and evaporate nearly to dryness. Take up with 5 cc. of concentrated nitric acid, dilute with water and filter into a flask. Through the same paper, filter the solution of the fusion which is taken up with dilute nitric acid; the silica is then well washed, burned and weighed. To the solution in the flask add 25 cc. ammonia, and then 25 cc. concentrated nitric acid, which should just redissolve the precipitate and leave the liquid slightly acid. Heat the solution in the flask to 85° exactly, and add 75 cc. ammonium molybdate solution and shake for five minutes. When it has stood for one-half hour, or until settled, filter through a 9 cm. Munktell's paper, which has been dried for one hour at 110° and weighed between watch-glasses as soon as taken from the oven. In presence of arsenic or titanium I follow Blair's acetate method, after obtaining together the main filtrate and that from the fused residue down to the basic acetate precipitate carrying the phosphorus. This is put in a small beaker, paper and all, and dissolved in a mixture of dilute nitric acid and hydrochloric acid by warming the beaker with its contents. Filter from the paper and evaporate for the expulsion of hydrochloric acid, filter into a 500 cc. flask and precipitate the phosphorus as above with ammonium molybdate solution at 85°. When necessary or desirable the yellow precipitate and paper are put into a small beaker, treated with dilute ammonia, the paper

and silica separated, and the phosphorus precipitated with magnesia mixture.

The yellow precipitate is washed well with 2 per cent. nitric acid solution, and, after the excess of moisture is removed with blotting-paper, dried in an oven at 110°, taking from the oven and weighing at once between the watch-glasses.

The ammonium molybdate solution is made by dissolving 200 grams molybdic acid in 500 cc. water with 500 cc. ammonia, and adding 2.5 liters of nitric acid (sp. gr. 1.20), and keeping in a warm place for twenty-four hours.

Determination of Manganese in Ores

In this determination the solution of the ore is prepared as in the case of the determination of phosphorus down to the filtration of the silica. If the quantity of the manganese is large the solution is made up to 500 cc. and an amount of the solution containing 1 gram of the ore is taken for the determination. In the case of ores low in manganese the same quantity of ore is weighed off but the whole of the solution is used for the determination. Evaporate with excess of strong nitric acid in a No. 4 beaker nearly to dryness twice. Then add 100 cc. strong nitric acid, heat to boiling, precipitate the manganese dioxide with potassium chlorate and boil for a few minutes. Remove from the lamp and cool. Filter through an asbestos plug and wash once with colorless nitric acid. When dry, transfer the asbestos and precipitate to the original beaker and wash filtering tube with concentrated hydrochloric acid and hot water, washing down the sides of the beaker with the same, using about 18 cc. hydrochloric acid. Heat, while shaking, over a lamp until manganese dioxide is entirely dissolved. Filter off the asbestos, receiving the solution in a half-liter flask. Wash well and make a basic acetate precipitate. Filter from this precipitate into a No. 6 beaker. Redissolve the precipitate with hydrochloric acid and repeat the basic acetate precipitation, filtering into the original solution. Make the solution in the beaker acid with acetic acid, heat to boiling and precipitate manganese with ammonium phosphate; boil until the precipitate is crystalline, stirring if necessary; then add 25 cc. ammonia, boil for a few minutes, remove from the heat and when settled filter

and wash with water about five times. Absorb the excess of water on a blotter and put the precipitate into a crucible. Char with the lid on, then uncover and burn white. Weigh as $Mn_2P_2O_7$.

Use all necessary precautions for lead and barium.

Determination of Silicon in Pig Iron

Weigh 0.9404 gram of iron, dissolve in 25 cc. of a mixture of 28 parts of nitric acid (sp. gr. 1.20) and 12 parts of dilute sulphuric acid (1 part water to 1 part acid). Evaporate in a 2 cm. evaporating dish, over a flame. When dry, raise the heat until copious fumes of sulphur trioxide escape. Cool, add a few cubic centimeters of dilute hydrochloric acid (3 parts acid to 5 parts water) and 25 cc. of hot water. Replace over the lamp until the solution is complete. Filter, wash the paper once with hot water, then once with dilute hydrochloric acid, and three or four times again with hot water; absorb the excess of water from the paper and the residue with blotting-paper. Place in a crucible and burn in the muffle, cool, weigh and divide by 2. Result= silicon.

Determination of Sulphur in Pig Iron and Steel

EVOLUTION METHOD

Weigh 5 grams of the sample, place into a half-liter flask, closed with a funnel tube and exit tube for gas which is connected with a tube extending to the bottom of a test-tube, 2.5 cm. wide and 25 cm. long. In the bottom of the test-tube is placed about one inch of ammoniacal solution of cadmium chloride. (This is made by dissolving 100 grams cadmium chloride in 500 cc. water, filtering into a 2 gallon bottle and adding 2.5 liters of water and enough ammonia to make up 5 liters.) After adding 1 inch of this cadmium chloride solution, fill the tube with water to two-thirds. To the drillings in the flask add 80 cc. dilute hydrochloric acid (3 parts acid to 5 parts water), place over an Argand burner and heat until quite warm; lower the flame until the solution is complete, then heat until steam drives all the gas from the flask. Disconnect the flask and pour the solution with the yellow sulphide from the test-tube into a No. 4 beaker. Wash out the tube with water and enough dilute hydrochloric acid to make the solution in the beaker acid and dissolve the sulphide. This is titrated immedi-

ately with a standard solution of iodine which has been standardized with a sulphur standard so as to read the percentage. Each 0.1 cc. = 0.001 per cent. sulphur in 5 grams of steel. While titrating be sure that all the sulphide is dissolved. In titrating, the beaker should be two-thirds full of solution.

GRAVIMETRIC METHOD

Weigh off 5 grams of metal, place into a No. 4 beaker, add a mixture of 5 cc. strong hydrochloric acid and 40 cc. strong nitric acid to the drillings at once. Heat until solution is complete, add 40 cc. strong hydrochloric acid, transfer to a No. 2 beaker or 12 cm. dish, and evaporate to hard dryness. Do not burn. Cool, add 30 cc. strong hydrochloric acid, dissolve and evaporate to the formation of a crust, add 10 or 12 drops of hydrochloric acid, dilute and filter into a No. 2 beaker. Wash well and fill the beaker three-fourths full, heat to boiling and precipitate with 3 cc. barium chloride solution (25 grams to 500 cc. water). Allow to stand over night on a warm plate or sand-bath, then evaporate to the formation of a crust, add a few drops of hydrochloric acid and dilute with water to about one-half beaker full; evaporate again to a crust, add a few drops of hydrochloric acid to redissolve and dilute to two-thirds full with cold water and allow to stand at room temperature over night. Filter through a double filter, Schleicher and Schüll, No. 590, 7 cm., wash well with hydrochloric acid and water, and burn in an open crucible. Purify this precipitate if necessary.

Determination of Phosphorus in Pig Iron and Steel

Dissolve 5 grams of the sample in a 12 cm. dish, using 60 cc. of nitric acid (sp. gr. 1.20) for steel, and 70 cc. for pig iron. When solution is complete, which will be in a few minutes for steel and in about twenty minutes to half an hour for pig iron, evaporate over an Argand burner with a watch-glass cover. When nearly dry lower the flame so that any iron that may have splashed up on the watch-glass may be redissolved and carried down into the dish. As soon as dry, remove the cover and heat over the lamp until all acid fumes are gone. Cool and add, in the case of pig iron, 35 cc. strong hydrochloric acid, and in the case of steel 30 cc.; replace the watch-glass and place over a low flame until complete solu-

tion, then raise the heat and evaporate as rapidly as possible with the cover on, until the solution is of a very dark color, and about to stick. Remove from the lamp, add 5 cc. strong nitric acid, shake until well mixed, and dilute with hot water to about 100 cc., washing off the watch-glass. Filter into a half-liter flask, washing paper and residue with 2 per cent. nitric acid and hot water. Add 25 cc. strong ammonia, shake and then redissolve with 25 cc. of strong nitric acid, leaving solution but slightly acid. Heat to 85° and add 75 cc. ammonium molybdate solution. Shake for five minutes. When well settled, filter through a 9 cm. Munktell filter, which has been dried at 110° for one hour and weigh between watch-glasses. Wash well with a 2 per cent. solution of nitric acid and dry at 110° for one hour. Weigh between watch-glasses. If arsenic or titanium be present, I follow Blair's acetate method after filtering from the residue down to the basic acetate precipitate carrying phosphorus. This precipitate is dissolved in a small beaker in a mixture of nitric and hydrochloric acids, applying heat. Filter from the paper, remove hydrochloric acid by evaporation, filter into a half-liter flask and precipitate with ammonium molybdate solution.

If desirable and necessary, dissolve the yellow precipitate in dilute ammonia, by putting paper and all into a beaker. Remove the paper and silica and precipitate as ammonium magnesium phosphate.

Determination of Manganese in Iron and Steel

COLOR METHOD

Weigh 0.2 gram iron or steel, place into a test-tube 2.5 cm. wide and 25 cm. long, and add 25 cc. nitric acid (sp. gr. 1.20). When solution is complete and all nitrous fumes are gone, add about 0.5 gram lead peroxide and boil for two minutes, cool in water and when settled compare the color with that of a standard which has been treated in the same way, the manganese in the standard having been determined gravimetrically. Dilute the standard to twice as many cubic centimeters as the percentage of manganese and divide cubic centimeters of all compared with it by 2. It takes some time for the solution of pig iron, and the heat of a very low flame should be used so as not to reduce the bulk of the fluid until solution is complete before adding the lead peroxide.

GRAVIMETRIC METHOD

Dissolve 5 grams of steel in 60 cc. nitric acid (sp. gr. 1.20), evaporate to a pasty condition in a No. 4 beaker, then add 100 cc. concentrated nitric acid, heat to boiling and precipitate manganese dioxide with potassium chlorate, filter through asbestos and proceed as with manganese in ores. Pig iron is treated in the same way as for phosphorus until filtering into a half-liter flask. For manganese it is filtered into a No. 4 beaker and evaporated twice with concentrated nitric acid to a pasty condition, then 100 cc. of concentrated nitric acid are added, and manganese dioxide precipitated with potassium chlorate. Proceed further in the same way as in the case of steel or ores.

Determination of Carbon in Steel and Iron

The steel or iron is dissolved in a solution of the double chloride of potassium and copper. This solution is prepared by dissolving 5 pounds of the salt in 6 liters of water, filtering first through paper and then through asbestos. Five per cent. of hydrochloric acid is added to this solution as it is used.

For 3 grams of steel use 180 cc. solution. If no stirring machine is at hand add the solution to the steel and stir frequently at first, allowing it to stand over night at the temperature of the room. Then warm on a sand-bath, stirring frequently until all copper is in solution. Cool and filter through a boat lined with asbestos which has been burned and ground up in water, decanting away the finer floating portion, leaving the fine asbestos, which, by shaking up in a bottle with water, can easily be transferred to the boat to make the felt. The solution of steel is filtered on felt, carefully washed with hydrochloric acid, then with warm water, until free from hydrochloric acid and copper. The boat with the carbon is dried at 80° or 90° for one hour, then burned in oxygen in a platinum tube which contains a coil of platinum gauze and copper oxide.

The combustion train is made up as follows:

First. Drying and purifying jars filled with caustic potash through which oxygen passes to the combustion tube; following the combustion tube is a U-tube filled on one side with anhydrous cuprous chloride and on the other with anhydrous copper sul-

phate, then a U-tube filled with strong sulphuric acid to close the lower part of the U. Following these are the absorption bulbs (Geissler's, potash with drying tube between the bulbs). The bulbs are filled with caustic potash solution of about 1.35 or 1.40 sp. gr.; the drying tube with calcium chloride. Connected with this is a Liebig bulb filled with sulphuric acid to serve as a trap. Then comes a calcium chloride tube, used as a protection, but not weighed. Great care is used in always keeping the potash bulbs with the calcium chloride tube filled with fresh material. A blank is always run before each day's series is begun, and this must agree with first weight to within 0.0005 gram. Where a number of combustions are to be made the Geissler and Liebig bulbs are weighed and then placed in the train for the next combustion, using the weight from the last one in beginning the next following, until the series or day's work is done. The joints are tested each time the apparatus is put together. One of the essential requirements for good results is cleanliness.

The tube is heated by lighting the burner nearest the absorption bulbs, and then, with oxygen flowing so that bubbles go at the rate of 3 per second, the burners are slowly lighted in succession, until the whole tube is red hot. The heating up requires about ten minutes. Keep red hot for fifteen minutes. Then turn off the oxygen and apply suction, maintaining the air flow at the same rate; lower the flames for a few minutes, then extinguish them. After suction has run for one-half hour the bulbs are ready to weigh.

Determination of Silicon in Steel

Five grams of steel are dissolved in 50 cc. nitric acid (sp. gr. 1.20); add 35 cc. dilute sulphuric acid (1 part sulphuric acid to 1 part water). Evaporate in a 12 cm. dish over an Argand burner with a watch-glass cover until bumping begins; remove the cover and stir with a rod until it grains or cakes. Dry until copious fumes escape. Cool, add about 20 cc. dilute hydrochloric acid and 100 cc. water, heat until solution is complete, filter, wash well with hydrochloric acid and hot water, burn and weigh.

III. Methods Used at the Laboratory of the Carnegie Steel Company, Lucy Furnace, Pittsburg, Penna.

By Robert Miller

Determination of Silica in Ores

Dissolve 1 gram of the ore in 40 cc. hydrochloric acid. Filter, wash, ignite, and fuse the residue with six times its weight of mixed carbonates of sodium and potassium. After fusion, introduce the crucible and contents into the filtrate. After the contents of the crucible are dissolved, remove the crucible and evaporate to dryness. Moisten with hydrochloric acid, add water, heat until all chlorides are in solution, filter, wash, ignite, and weigh as silica.

Determination of Iron in Ores

One gram of the ore is dissolved in 40 cc. hydrochloric acid. Reduce with stannous chloride, add 60 cc. mercuric chloride solution (all at once), and stir vigorously. Titrate with potassium dichromate solution, using potassium ferricyanide as an indicator.

SOLUTIONS

Stannous Chloride Solution.—120 grams of the salt are dissolved in 1500 cc. of hydrochloric acid and 2 liters of water.

Mercuric Chloride Solution.—Fifty grams of the salt are dissolved in 1 liter of water.

Determination of Iron in Manganese Ores

One gram of the ore is dissolved in 40 cc. hydrochloric acid. Filter and evaporate to a small volume, add ammonia water in slight excess, boil, and filter. Wash the precipitate with hot water, dissolve in dilute sulphuric acid (1:5), filter through a zinc reductor, and titrate the iron in the filtrate with standard potassium permanganate solution.

Determination of Aluminum Oxide in Ores

The hydrochloric acid solution of 1 gram of the ore is nearly neutralized with ammonia. Add 20 cc. of a 10 per cent. solution of ammonium phosphate and then hydrochloric acid sufficient to redissolve any precipitate formed. The solution should be clear and of a light yellow color. Add 10 grams of sodium thiosulphate and stir until all iron is reduced and the precipitation of sulphur has just begun. Add at once 15 cc. of acetic acid (sp. gr. 1.05), and boil until sulphur dioxide is nearly all expelled. Filter (using suction), wash with boiling water, ignite, and weigh as $AlPO_4$. Multiply this weight by 0.4185 and obtain Al_2O_3.

Determination of Manganese in Iron Ores

Dissolve 1 gram of the ore in 40 cc. hydrochloric acid, transfer the solution to a flask of about 750 cc. capacity, add zinc oxide stirred up in water, dilute to 0.5 liter, boil, and titrate with standard potassium permanganate solution.

Determination of Manganese in Blast-Furnace Cinder

Dissolve 0.5 gram of the cinder in dilute hydrochloric acid (1:1), with addition of a few crystals of potassium chlorate. Boil until the chlorine is expelled, add zinc oxide, and determine manganese by titration with standard potassium permanganate solution.

Determination of Phosphorus in Iron Ores

Dissolve 3 grams of the ore in 60 cc. hydrochloric acid (sp. gr. 1.20), evaporate to 15 cc., dilute the solution, filter and wash. Ignite the residue and treat with hydrofluoric acid and a few drops of sulphuric acid. Evaporate until fumes are produced, take up with dilute hydrochloric acid and add to the filtrate from the insoluble matter. Proceed further as described for the determination of phosphorus in pig iron.

Determination of Manganese in Manganese Ores

GRAVIMETRIC METHOD

Dissolve 1 gram of the ore in 30 cc. hydrochloric acid, dilute with 40 cc. water, filter, ignite the residue and treat with hydrofluoric and sulphuric acids. Heat until sulphuric acid fumes appear, dissolve in dilute hydrochloric acid (1:3), and add the solution

obtained to the main solution. Evaporate to dryness, add 100 cc. nitric acid (sp. gr. 1.42), boil until nitrous fumes are expelled, and add potassium chlorate, a few crystals at a time, until the characteristic explosion occurs. The beaker will now be cleared of chlorine, which, before the explosion, collects above the boiling solution. Boil for a few seconds longer and filter through an asbestos plug. Wash with hot nitric acid (sp. gr. 1.42) free from nitrous acid. Dissolve the oxide on the plug in hydrochloric acid, using a few drops of acid ammonium sulphite solution to aid in reduction, and also to precipitate any barium. Wash with water and boil the filtrate until all sulphur dioxide is expelled. (If a precipitate of barium sulphate separates, filter.) Add ammonia water until the solution smells very faintly, and then 5 cc. ammonium acetate solution. Boil and filter off any basic ferric acetate, add to the filtrate 40 cc. of a 20 per cent. solution of ammonium phosphate, acidify with hydrochloric acid, boil, and precipitate manganese by ammonia water added drop by drop until the solution smells strongly of ammonia. The precipitate should now be of a granular character. Filter (using suction), wash with boiling water, ignite and weigh as $Mn_2P_2O_7$.

VOLUMETRIC METHOD

Obtain a solution of 1 gram of the ore as in the preceding method, add zinc oxide and proceed as in the case of the determination of manganese in ferromanganese.

Determination of Silicon in Pig Iron and Spiegel

Dissolve 1 gram of the metal in 50 cc. of "silicon mixture." Evaporate until fumes of sulphuric acid escape. Take up with 60 cc. dilute hydrochloric acid (1:5), boil, filter (using suction), wash with dilute hydrochloric acid (1:3) and then with hot water. Ignite and weigh as silica. This weight multiplied by 0.47 gives the silicon. The "silicon mixture" is made up of 2 liters of water, 1 liter of nitric acid (sp. gr. 1.42), and 350 cc. strong sulphuric acid.

Determination of Silicon in Ferromanganese

Dissolve 1 gram of the metal in 30 cc. hydrochloric acid and evaporate to dryness. Take up with 50 cc. hydrochloric acid

(1:3), filter (using suction), wash with hydrochloric acid, then with water, ignite, and weigh.

In the case of silicospiegel and the ferrosilicon metal is first powdered in a steel mortar so as to pass through bolting-cloth of 150 meshes to the inch. One gram is heated with 80 cc. aqua regia for five minutes; 15 cc. of dilute sulphuric acid (1:3) are then added. Evaporate until dense fumes arise and proceed as in the case of silicon in pig iron. This method yields silica in pure white form, which is wholly volatile on treatment with hydrofluoric acid.

Determination of Phosphorus in Pig Iron and Steel

From 1 to 3 grams of the sample, according to the percentage of phosphorus present, are dissolved in nitric acid (sp. gr. 1.16). The solution is evaporated to dryness and the residue baked. Dissolve the residue in hydrochloric acid. Evaporate the solution to a volume of about 15 cc., filter and wash. Neutralize with ammonia water, redissolve the precipitate in nitric acid, heat the solution to 80° C. and add 50 cc. molybdate solution. Shake for five minutes, filter and wash the precipitate with a solution of acid ammonium sulphate. Dissolve the precipitate in 25 cc. dilute ammonia water (1:4). The filtrate is received in the flask in which the precipitation was made. Make the filtrate up to about 200 cc. and add 15 cc. concentrated sulphuric acid; reduce by filtering through a zinc reductor and titrate with standard permanganate solution.

The iron factor of the permanganate multiplied by 0.1581644 gives the phosphorus factor.

The Acid Ammonium Sulphate Solution is made by adding 15 cc. of ammonia water (sp. gr. 0.90) to 1 liter of water and then adding 25 cc. of concentrated sulphuric acid.

Molybdate Solution.—Wood's formula is used. Blair's "Chemical Analysis of Iron," third edition, p. 109.

Determination of Sulphur in Pig Iron and Steel

GRAVIMETRIC METHOD

In case of pig iron, silicospiegel and ferrosilicon, 5 grams of the metal are treated with a mixture of 50 cc. nitric acid (sp. gr. 1.42)

and 10 cc. concentrated hydrochloric acid. In the case of silicospiegel and ferrosilicon, after the action has ceased, hydrofluoric acid is added in portions of a few drops at a time to aid in the solution of the metal. Evaporate to dryness. Dissolve the residue in 60 cc. hydrochloric acid and evaporate again to dryness. Take up with hydrochloric acid, concentrate to a small bulk, filter, and precipitate with barium chloride solution. Allow the precipitate to stand over night, filter, wash, ignite, and weigh as $BaSO_4$.

EVOLUTION METHOD

Payne's method of making up the iodine solution is used. For convenience, the iron factor of the permanganate solution is divided into 1.75 to give the number of cubic centimeters of permanganate solution necessary to make 1 liter of iodine solution; 10 grams of potassium iodide are placed in a liter flask with 15 cc. dilute sulphuric acid and the requisite number of cubic centimeters of permanganate solution added, shaking the flask during the addition. Now make up to 1 liter. One cc. of this solution corresponds to 0.01 per cent. of sulphur when 5 grams of metal are used for a determination.

Determination of Manganese in Pig Iron

Volhard's method is used as described in Blair's "Chemical Analysis of Iron," third edition.

Determination of Manganese in Spiegel and in Ferromanganese

Dissolve 1 gram of the metal in 40 cc. nitric acid (sp. gr. 1.16). Transfer to a liter flask and precipitate the iron by zinc oxide, stirred up in water. Dilute to the 1 liter mark. Mix well by pouring into a beaker and back. Filter 200 cc. into a flask of 750 cc. capacity, dilute to 500 cc. and titrate with permanganate solution. The gravimetric method is used as a check. In case of silicospiegel, hydrofluoric acid is added from time to time during the solution of the metal. About 16 drops in all are ordinarily required.

Determination of Nickel in Steel

Nickel is determined according to the method described by Chase. Blair's "Chemical Analysis of Iron," third edition. Appendix.

IV. Methods Used at the Laboratory of the Monongahela Furnace, McKeesport, Penna.

By Frederick Crabtree

Determination of Silica in Ores

One-half to 1 gram of the ore (powdered to pass through a 100-mesh sieve) is fused with sodium carbonate, the fusion dissolved in dilute hydrochloric acid, and the solution evaporated to dryness in a 15 cm. Royal Meissen evaporating dish. When the residue is thoroughly dry, dilute hydrochloric acid is added and the mixture boiled until the iron salt is dissolved. The solution is then filtered, the silica washed with hot water, ignited, and weighed. When considered advisable the silica, after weighing, is treated with hydrofluoric acid and a few drops of strong sulphuric acid, and the silica determined by loss in weight on ignition.

Determination of Iron in Ores

One-half gram of the ore is placed in a beaker of about 60 cc. capacity. Add 35 to 40 cc. of strong hydrochloric acid and heat for several hours (usually over night) on the steam-bath. A few drops of stannous chloride solution may be added to hasten the solution. When ready for the titration the contents of the beaker are heated to boiling and examined to ascertain whether the residue is white; a slight excess of stannous chloride solution is added, the mixture placed in a beaker of 600 cc. capacity and diluted with about 300 cc. of cold water. About 25 cc. of a cold saturated solution of mercuric chloride are added and the solution titrated with a solution of potassium dichromate containing about 4.38 grams of the salt in 1 liter.

Determination of Phosphorus in Ores

2 to 5 grams of the ore are digested with 75 to 150 cc. of strong hydrochloric acid and the solution evaporated to hard dry-

ness. About 100 cc. of strong hydrochloric acid are poured on the residue and the mixture boiled until the solution is concentrated to about half that volume. The solution is then diluted with water, filtered, and washed with hot water into a 500 cc. Erlenmeyer flask. The insoluble residue is ignited, fused with a mixture of sodium and potassium carbonates, dissolved in dilute hydrochloric acid and evaporated to dryness. The residue is treated with dilute hydrochloric acid and filtered, and from the filtrate the iron and phosphoric acid are precipitated by the acetate method. This precipitate is next dissolved in hydrochloric acid and filtered into the main solution of the ore. The main solution is then neutralized by ammonia, a slight excess of nitric acid added to dissolve the precipitate produced and the solution brought to a temperature of 75° C., when 40 cc. of molybdate solution are added. After shaking by hand for a few seconds the yellow precipitate is allowed to settle. It is filtered while still warm, washed with cold water, and the phosphorus determined by the acidimetric acid.

Determination of Manganese in Ores

The filtrate from the silica determination is evaporated nearly to dryness, 100 cc. of strong nitric acid are added, and the solution boiled until the hydrochloric acid is about all expelled. The manganese is then precipitated by potassium chlorate, and, after filtration through asbestos, solution in hydrochloric acid and separation of the iron as basic acetate, is determined as pyrophosphate in the usual way.

For routine work with ordinary ores low in manganese, 1 gram is dissolved in hydrochloric acid and the manganese determined by titration with potassium permanganate as in the case of pig iron.

Determination of Silicon in Pig Iron

One gram of the drillings is dissolved in 20 to 25 cc. of nitric acid (sp. gr. 1.20) and 8 to 10 cc. of dilute sulphuric acid (1:3), and the solution evaporated in a 12 cm. Royal Meissen porcelain dish until sulphuric acid fumes are copiously evolved. The residue is treated with dilute hydrochloric acid and the mixture boiled; the residue is filtered off and washed with hot water and dilute hydrochloric acid, ignited and weighed as SiO_2.

Determination of Sulphur in Pig Iron

The evolution method is ordinarily used, receiving the hydrogen sulphide in a dilute ammoniacal solution of cadmium chloride, and titrating with iodine solution without filtration.

Determination of Phosphorus in Pig Iron

Four grams of Bessemer pig iron are dissolved in 100 cc. of dilute nitric acid (sp. gr. 1.13). Evaporate to dryness in a 15 cm. dish. After baking for about twenty-five minutes, the residue is dissolved in strong hydrochloric acid to which eight or ten drops of hydrofluoric acid have been added. When the iron is all dissolved the solution is filtered into a 500 cc. Erlenmeyer flask. The process is then continued exactly as in the case of ores.

Determination of Manganese in Pig Iron

One gram of the pig iron is dissolved in dilute nitric acid, 25 cc. of water and 15 cc. of nitric acid (sp. gr. 1.42); the solution is evaporated nearly to dryness, diluted with water, a slight excess of zinc oxide being mixed with the water added, and the volume made up to 500 cc. After thorough mixing, the precipitate is allowed to settle; 250 cc. of the supernatant liquid are decanted and titrated hot by potassium permanganate.

Determination of Sulphur in Steel

The evolution method is used as described in the case of pig iron.

Determination of Phosphorus in Steel

Four grams of the drillings are dissolved in 100 cc. of dilute nitric acid (sp. gr. 1.13), potassium permanganate added, the precipitated oxide of manganese is dissolved in hydrochloric acid, the solution made alkaline with ammonia, and the determination finished as in the case of iron ores and pig iron.

Determination of Manganese in Steel

COLOR METHOD

0.2 gram of steel (the steel examined at this laboratory is soft and usually contains from 0.25 to 0.45 per cent. manganese) is dissolved in 15 cc. of dilute nitric acid (sp. gr. 1.20). When the solution is clear and free from lower oxides of nitrogen, 15 cc. of

water are added. The solution is boiled, lead peroxide added, and the boiling continued for two minutes. A little more lead peroxide is then added, the flasks are removed from the hot plate, and the lead peroxide is caused to subside by help of a centrifugal machine. The color is then compared with that of the standard steel accompanying each batch of determinations.

Determination of Carbon in Steel

CHROMIC ACID COMBUSTION METHOD

For dissolving the steel a solution of copper potassium chloride acidified with hydrochloric acid is used. The solution of the steel is hastened by shaking or agitation.

In the combustion process the following train is used after the reversed condenser:

First, a small empty bottle; *second;* pyrogallol solution as recommended by the Committee on International Standards, and containing 0.2 gram pyrogallol, 5 grams potassium oxalate, 3 grams sodium chloride, 0.2 gram sulphuric acid, and water sufficient to make the volume 20 cc.; *third,* silver sulphate solution; *fourth,* strong sulphuric acid; *fifth,* a weighed potash bulb; *sixth,* a small weighed flask containing sulphuric acid to retain any moisture that might be carried over from the potash bulb; *seventh,* a guard tube containing sulphuric acid.

V. Methods Used at the Laboratory of the Pennsylvania Malleable Iron Company, McKees Rocks, Penna.

By H. E. Diller

Analysis of Iron and Manganese Ores.

The method described in Morgan's "Tables for Quantitative Metallurgical Analysis," is used.

Determination of Silicon in Iron and Steel

Dissolve 0.9404 gram of iron drillings in 30 cc. of a mixture of nitric and sulphuric acids, in a 10 cm. flat-bottomed evaporating dish. Evaporate on a hot plate until white fumes are given off. Allow to cool, take up in 20 cc. hydrochloric acid (1:1), and digest at 50° C. for five minutes. Add 30 cc. water and bring to a boil. Filter through a 9 cm. ashless filter, with the aid of suction. Wash well with hot water, ignite, and weigh. Divide the weight by 2 and multiply by 100 to get the percentage of silicon.

For steel weigh out 4.702 grams of drillings and add 90 cc. of acid mixture. Proceed as in pig iron, taking up with 50 cc. hydrochloric acid, and multiplying by 10 to get the percentage of silicon.

The nitric and sulphuric acid solution is made by diluting 250 cc. sulphuric acid (sp. gr. 1.83) with 800 cc. water, and 650 cc. nitric acid (sp. gr. 1.42) with 650 cc. water. When cool add the nitric to the sulphuric acid.

Determination of Phosphorus in Iron and Steel

Dissolve 1.63 grams of iron drillings in 50 cc. of nitric acid (sp. gr. 1.13). Bring to a boil and filter into a 200 cc. Erlenmeyer flask, washing three times with hot water. Boil, add solution of potassium permanganate, drop by drop, until a brown precipitate is formed. Boil a few minutes. Take away from the heat and add ferrous sulphate crystals until the solution becomes clear. Boil for

two minutes, cool to about 80° C., and add 50 cc. molybdate solution previously heated to 40° C. Allow to stand for twenty minutes with occasional shaking. Filter through a tared 7 cm. filter-paper. Wash three times with a 3 per cent. solution of nitric acid, and once with alcohol. Dry in a steam-bath and weigh before it is cool.

In case of steel dissolve 1.63 grams of drillings in 30 cc. nitric acid (sp. gr. 1.20) in a 200 cc. Erlenmeyer flask and proceed as in case of pig iron but without filtering.

The molybdate solution is made as described in Blair's "Chemical Analysis of Iron," third edition.

Determination of Sulphur in Iron and Steel

EVOLUTION METHOD

Dissolve 3 grams of the drillings in 60 cc. hydrochloric acid (1:1) and absorb the hydrogen sulphide which is evolved, in a dilute ammoniacal solution of cadmium chloride. This is acidulated with 30 cc. hydrochloric acid (1:1) and titrated with iodine solution.

The iodine solution is standardized by samples B and C of the American Foundrymen's Association.

The method described in the appendix of Blair's "Chemical Analysis of Iron," is also used.

Determination of Carbon in Iron and Steel

I use the color method except when very accurate work is required, being careful to have the standards as near as possible to the sample.

Determination of Graphite in Pig Iron

The method described by George T. Dougherty is used.[1] One gram of the iron is dissolved in 60 cc. nitric acid (sp. gr. 1.135). Heat gently until all is in solution and boil for a few minutes. Do not evaporate or use stronger or weaker acid. The quantity of acid used should not be less than nor exceed the amount specified as there is danger that the silicic acid formed may gelatinize and increase the proportion of insoluble residue. Have ready a weighed Gooch crucible. Place a disk of ashless filter-paper

[1] *Iron Age*, May, 1899; *Chemical News*, September 8, 1899.

(about the size of a dime) in the crucible and weigh again. Adjust the crucible with its paper disk in a filter-bottle connected with a filter-pump and pour some water into the crucible to cause the disk to adhere firmly to the bottom of the crucible. Now filter the solution of the iron and wash five times with hot 10 per cent. nitric acid and once or twice with hot water. The operation of filtering and washing need not occupy more than ten or fifteen minutes. Dry at 115°-120° until the weight is constant. The weight of the insoluble residue is thus ascertained. Burn over a Bunsen burner. The residue consists of silicon (silica having been retained in solution as silicic acid during the solution of the iron) and a minute quantity of iron oxide which has been found to vary from 0.0005 to 0.004 gram. The quantity of hydration water in the insoluble residue is too minute to require that allowance should be made for it. The paper disks used are so small that they may be regarded as uniform in weight; they filter better than asbestos, and permit of more rapid combustion of the graphite.

Determination of Manganese in Iron and Steel

COLOR METHOD

Weigh 200 mg. of iron or steel into a 60 cc. flask, and add 20 cc. of nitric acid (sp. gr. 1.20). When dissolved, boil gently for five minutes, remove, and pour the solution into a 100 cc. graduated cylinder. Wash out the flask three times with water, and finally dilute to the 100 cc. mark. Pour the contents into a 4 oz. precipitating jar and mix by pouring into a cylinder or jar at least three times. Draw off 25 cc. with a pipette into the flask in which the solution was made, add 6 cc. nitric acid (sp. gr. 1.20) from a burette, place on a hot plate together with a standard in which the manganese is exactly known and which has been treated exactly like the steel, and when almost boiling add 0.5 gram lead peroxide, measured approximately on a small glass spatula, and boil for three minutes. Remove, place in a cooling bath, and allow the lead peroxide to settle, which usually requires fifteen minutes. Decant the solution into a comparison tube and compare with the standard properly diluted as for color carbon determination.

VI. Methods Used at the Laboratory of the Carbon Steel Company, Pittsburg, Penna.

By G. O. Loeffler

Determination of Silica in Ores

Fuse 1 gram of ore with 5 grams of sodium carbonate; dissolve in hydrochloric acid. Evaporate to dryness, take up with hydrochloric acid and water, and filter. Burn and weigh as SiO_2.

Determination of Iron in Iron Ores

Weigh 0.5 gram of the finely ground ore, place into a 150 cc. Erlenmeyer flask, add 10 cc. of hydrochloric acid and boil gently until the acid appears to have no further action. Filter and if the residue is not white treat with sulphuric and hydrofluoric acids. Fuse with sodium carbonate. Digest the fusion with water, filter and dissolve any residue remaining on the filter in hydrochloric acid, receiving the filtrate in the beaker (360 cc. capacity) containing the main solution. Heat the solution to boiling, add stannous chloride until the ferric chloride is reduced, add 15 cc. of a saturated solution of mercuric chloride and titrate with standard solution of potassium dichromate.

Determination of Phosphorus in Ores

Dissolve 2 to 5 grams of the sample in 40 cc. of hydrochloric acid and a little nitric acid. Evaporate to dryness, take up in hydrochloric acid, evaporate to a small bulk and filter into a 250 cc. Erlenmeyer flask. Fuse the residue, dissolve in hydrochlric acid, evaporate to dryness, take up and filter into the main solution. Add ammonia in slight excess, dissolve in nitric acid, precipitate with molybdic solution, and proceed as in case of steel.

Determination of Sulphur in Ores

Fuse 1 gram of ore with 5 grams of sodium carbonate and 0.5 gram of potassium nitrate, dissolve in water, and filter. Acidify

the filtrate with hydrochloric acid, evaporate to dryness, take up in a few drops of hydrochloric acid and water, filter, dilute to 150 cc., add 5 cc. of barium chloride, and boil for fifteen minutes; allow the precipitate to settle, filter, burn, and weigh as $BaSO_4$.

Determination of Manganese in Ores

Williams' method is used. See Blair's "Chemical Analysis of Iron," third edition, p. 120.

Determination of Silicon in Pig Iron

Dissolve 0.4702 gram in 15 cc. sulphuric acid (1:3), in a 150 cc. beaker, heat gently until the iron is dissolved, evaporate to fumes, cool, add 40 cc. water and 5 cc. hydrochloric acid, and boil until all sulphates are in solution. Filter. Burn in a platinum crucible, using oxygen and a blast-lamp, and weigh.

Determination of Phosphorus in Pig Iron

The method is the same as is used in case of steel, except that the drillings are weighed in a 150 cc. beaker, and after solution the graphite and silica are filtered off.

Determination of Sulphur in Pig Iron

The method described for steel is used.

Determination of Manganese in Pig Iron

See the method described in the case of steel.

Determination of Phosphorus in Washed Metal

Dissolve 2 grams of metal in a 15 cm. evaporating dish in 40 cc. of nitric acid (sp. gr. 1.20), evaporate to dryness and bake on a hot plate for twelve hours or burn over a Bunsen flame for thirty minutes. Take up in hydrochloric acid, evaporate to a small bulk, dilute and filter into a 250 cc. Erlenmeyer flask, add ammonia in slight excess, then nitric acid until the precipitate is dissolved and a few cubic centimeters in excess. Heat to 85°, precipitate with 45 cc. of molybdate solution, filter and finish as in case of steel.

This method is also used for pig iron high in combined carbon.

Determination of Silicon in Steel

Dissolve 4.702 grams of steel in a 12½ cm. porcelain evaporating dish in 40 cc. hydrochloric acid, heat gently until solution is com-

plete and then evaporate to dryness and bake on the hot plate for one hour. Take up in 20 cc. hydrochloric acid, heat until all iron salts are dissolved, dilute with water and boil for a few minutes, filter, wash with water twice, then with hydrochloric acid (1:3), and then wash free from acid. Burn in a platinum crucible, heat with blast, cool, and weigh; add a drop of sulphuric acid and a few drops of hydrofluoric acid, evaporate to dryness, heat gently to expel sulphuric acid, and finally over a blast. Cool and weigh.

Determination of Sulphur in Steel

EVOLUTION METHOD

Weigh 5 grams of the drillings in a half-liter flask, close with a rubber stopper fitted with a thistle and delivery tube, run the delivery tube into a cooling tube, and then into a 250 cc. beaker containing 5 cc. of an ammoniacal solution of cadmium chloride and about 150 cc. of water. Add to the flask 50 cc. of hot hydrochloric acid (1:1), and after the violent action has ceased place a low flame under the flask; heat gently until all the steel is dissolved, raise the heat, and boil the solution until the gas ceases to bubble through the solution; disconnect the delivery tube, add to the beaker containing the cadmium sulphide, a few drops of starch paste and about 10 cc. of hydrochloric acid and titrate with standard iodine solution.

SOLUTIONS

Cadmium Chloride Solution is made by dissolving 50 grams of the salt in 1 liter of water and adding 1.5 liters of ammonia.

Iodine Solution.—Dissolve 2.017 grams of potassium permanganate in 100 cc. of water. Dissolve 30 grams of potassium iodide in a liter flask and add 20 cc. of sulphuric acid (1:3); pour into this the permanganate previously dissolved and dilute to 2 liters.

Starch Solution.—Boil 100 cc. of water, add about 1 gram of starch, mixed with a few cubic centimeters of water, and boil for a few minutes.

Determination of Phosphorus in Steel

Dissolve 2 grams of the drillings in 70 cc. nitric acid (sp. gr. 1.13) in a 250 cc. Erlenmeyer flask. After the solution is

complete, boil until all nitrous fumes disappear, add 20 cc. of potassium permanganate; boil until the pink color disappears and the brown oxide of manganese is precipitated; allow the flask to cool for a minute, add 0.2 gram sugar and heat until the solution becomes clear. Add 10 cc. of ammonia, heat or cool to 85° C., add 45 cc. of molybdate solution, and shake without a stopper for five minutes, giving the flask a circular motion. Allow to stand for one-half hour and filter through a 9 cm. filter. Wash five times with 1 per cent. nitric acid and five times with potassium nitrate. Place the filter into the flask in which the precipitation was made, after rinsing out all acid with water; add 20 cc. of water and 10 cc. of sodium hydroxide solution, break up the filter with a glass rod and stir until the precipitate is dissolved, clean off the rod with water, add 3 drops of phenolphthalein, and run in standard nitric acid until the pink color just disappears.

SOLUTIONS

Potassium Permanganate Solution.—Five grams of crystals are dissolved in 1 liter of water.

Molybdate Solution.—500 grams of molybdic acid are dissolved in 1200 cc. of water and 700 cc. of ammonia. Add 300 cc. of nitric acid and allow to cool. Pour this into a solution of 2 liters of nitric acid and 4.8 liters of water.

Potassium Nitrate Solution.—Dissolve 10 grams of potassium nitrate crystals in 1 liter of water.

Standard Sodium Hydroxide Solution.—Dissolve 150 grams in 1 liter of water, add barium hydroxide until the carbonate is all precipitated, allow the precipitate to settle, siphon off the clear liquid, and dilute to 2 liters. Use 200 cc. of this solution and dilute to 2 liters.

Standard Nitric Acid.—Dilute 80 cc. nitric acid (sp. gr. 1.40) to 8 liters.

Phenolpthalein Solution.—Dissolve 0.5 gram of the powder in 200 cc. of 95 per cent. alcohol.

Determination of Manganese in Steel

COLOR METHOD

Dissolve 0.1 gram of the drillings in 30 cc. nitric acid (sp. gr.

1.13) in a 10″ x 1″ tube, boil until all nitrous fumes disappear, add 0.5 gram of lead peroxide, boil for one and one-half minutes, and allow to stand in water until the lead has settled. Pour into a comparison tube and compare the color with that of a standard steel treated in the same way as the sample.

Determination of Carbon in Steel

See Blair's "Chemical Analysis of Iron," second edition, p. 151, (2).

Determination of Nickel in Steel

ETHER METHOD

Dissolve 1 gram of steel in 30 cc. hydrochloric acid (1:1) in a porcelain evaporating dish. After solution is complete, add a few drops of nitric acid and boil down to about 15 cc.; cool, transfer the solution into a 250 cc. separatory funnel (using hydrochloric acid (1:1) for rinsing), add 40 cc. of ether, insert the stopper, and shake for about one minute. Allow to stand until the ether separates, run off the lower (watery) layer into a 250 cc. beaker, add 10 cc. hydrochloric acid to the funnel and shake. Allow the washings to separate and add them to the main solution in the beaker. Heat gently until the ether is driven off, add a few drops of nitric acid, boil, add ammonia in excess, boil, and filter. Dissolve the precipitate of iron in dilute hydrochloric acid and repeat the precipitation. Filter, combine the filtrates, add acetic acid until acid, then make just alkaline with ammonia, pass hydrogen sulphide through the solution for ten minutes, add acetic acid until acid, and boil for two or three minutes. Filter, wash, burn in a porcelain crucible, and finally heat over the blast-lamp. Weigh as NiO. $NiO \times 0.7858 = Ni$.

Determination of Chromium in Steel

The method of A. G. McKenna is used. Steels having a high percentage of chromium are best dissolved in a mixture of nitric and hydrochloric acids and the hydrochloric acid afterwards removed by evaporation with nitric acid, before adding potassium chlorate.

Determination of Iron in Open Hearth Cinder

Weigh off 0.5 gram of the cinder into a platinum dish, add 15 cc. hydrochloric acid and 3 or 4 cc. hydrofluoric acid, heat until

dissolved, and evaporate to small bulk to get rid of hydrofluoric acid. Rinse into a 250 cc. beaker, reduce with stannous chloride, cool, add 15 cc. of mercuric chloride solution and titrate with potassium dichromate.

Determination of Phosphorus in Open Hearth Cinder

Dissolve 5 grams of the cinder in hydrochloric acid and nitric acid, evaporate to dryness, take up in hydrochloric acid and filter. Burn the precipitate, fuse with sodium carbonate and potassium nitrate. Dissolve in water, acidify with hydrochloric acid, evaporate to dryness and filter into the main solution. Add ammonia in slight excess, redissolve in nitric acid having a little in excess, and precipitate with molybdate.

Determination of Manganese in Open Hearth Cinder

Proceed as in the determination of iron, and after transferring into a beaker add nitric acid and boil down to a small bulk; add 40 cc. of nitric acid, boil; if no fumes appear add potassium chlorate crystals, and proceed with Williams' method. (Blair's "Chemical Analysis of Iron," third edition, p. 120).

VII. Methods Used at the Laboratory of the Carnegie Steel Company, Duquesne, Pa.

By J. M. Camp

Determination of Silica in Ores

Five grams of the finely ground ore, dried at 100° C. for one hour, are placed in a 12 cm. porcelain dish with a watch-glass cover; 50 cc. concentrated hydrochloric acid, are added and the solution evaporated to dryness on a sand-bath. Add 15 or 20 cc. strong hydrochloric acid, warm, and, when all is in solution, evaporate until a crust of ferric chloride separates. This is dissolved by adding 10 cc. strong nitric acid and the solution diluted to about 75 cc. and filtered into a half-liter flask. The residue is fused with the mixed carbonates of potassium and sodium. The fused mass is digested in hot water, hydrochloric acid added, and the whole evaporated to dryness. Moisten with hydrochloric acid (1 part acid, 2 parts water), dilute, and filter into the flask containing the original filtrate, keeping the liquid as concentrated as possible. The silica so obtained is ignited and weighed and needs no further purification.

Determination of Phosphorus in Ores

A slight excess of strong ammonia is added to the combined filtrates as obtained in the silica determination. This is followed by the addition of a slight excess of strong nitric acid (about 5 cc.), and the process is then continued in the same manner as in the case of pig iron and steel.

The following rapid method is also used: 5 grams of the ore are dissolved in 50 cc. concentrated hydrochloric acid in a 12 cm. covered dish by boiling for thirty minutes, or until the iron is all in solution. Dilute with an equal volume of water and filter into another dish of the same size. The residue is fused with the mixed carbonates. The fused mass is digested with hot water, and the solution evaporated, with addition of hydrochloric acid,

in the dish in which the ore was originally dissolved. The two solutions are brought to dryness on the sand-bath. 15 cc. strong hydrochloric acid are added to the dish containing the residue of the original filtrate and the dish is heated until ferric salt is wholly dissolved and the excess of hydrochloric acid is expelled, as indicated by the first appearance of solid ferric chloride. This is dissolved by adding 10 cc. strong nitric acid and warming. Dilute with cold water to about 75 cc. and filter into a 500 cc. flask. The evaporated solution from the fusion is taken up with hydrochloric acid, water is added and the solution is filtered into the same flask with the last filtrate. The process is then continued as before.

Determination of Iron in Ores

Weigh 1 gram of the finely ground ore (dried at 100° C.) place into a No. 0 beaker, add 20 cc. strong hydrochloric acid, and for a 60 per cent. ore, 5 cc. of the stannous chloride solution. Cover with a watch-glass and heat on a sand-bath until all but the silicious residue is dissolved. While still hot add stannous chloride solution, drop by drop, until the color due to ferric chloride disappears, and then 1 drop in excess. Transfer to a No. 4 beaker containing about 300 cc. of cold water, add 10 cc. mercuric chloride solution, and stir; allow to stand about one minute and then titrate with potassium dichromate solution, until a drop of the solution added to a drop of potassium ferricyanide solution on a porcelain plate exhibits no green color on standing one-half minute. The number of cubic centimeters of potassium dichromate solution used gives directly the percentage of iron in the ore.

In case the residue from the solution of the ore is suspected to contain iron it is fused with the mixed carbonates of sodium and potassium, the fusion is placed into water, and the solution obtained is filtered. The ferric oxide on the filter is dissolved in hydrochloric acid and the solution is added to the original solution previous to the titration.

SOLUTIONS

Stannous Chloride Solution is made by dissolving 300 grams of the salt in a mixture of 500 cc. strong hydrochloric acid and 500 cc. water. One cc. will reduce about 0.1 gram of iron.

Mercuric Chloride Solution is made by dissolving 50 grams of the salt in 1 liter of water.

Potassium Ferricyanide Solution is made by dissolving about 0.05 gram of the salt in 50 cc. water.

Potassium Dichromate Solution is made by dissolving 8.9 grams of the salt in 1 liter of water. Standardize with iron wire, standard steel or an iron ore and dilute so that 1 cc. corresponds to 1 per cent. of iron when 1 gram of an ore sample is used for analysis. After dilution test the strength of the solution with the standard steel or ore.

Determination of Manganese in Ores

The agate mortar sample is dried for one hour at 100° C., allowed to cool, and five grams weighed off into a 12 cm. porcelain dish with watch-glass cover, 50 cc. strong hydrochloric acid are added, and the solution allowed to go to dryness on the sand-bath.

The residue is moistened with dilute hydrochloric acid (1 part acid, 2 parts water), diluted, heated till all is in solution, and filtered into a 500 cc. graduated flask. The residue is burned and fused with five to ten times its weight of the mixed carbonates of potassium and sodium. If fusion shows presence of manganese it is dissolved in hot water, acidified with hydrochloric acid, evaporated to dryness, taken up as before, and filtered into the same flask with the original filtrate.

The solution is cooled, diluted to the mark, and, with the aid of an exactly agreeing pipette, 100 cc. (equal to one gram of ore) are taken as many times as desired into No. 4 beakers, 30 cc. strong nitric acid added, and the solution evaporated to about 10 or 15 cc.; 75 cc. strong nitric acid are now added and the solution heated to boiling, and, while boiling, an excess of potassium chlorate is added in small portions. The solution is boiled for a few minutes after the final puff. Cool, and filter through a purified asbestos plug with the aid of suction. The beaker and plug are washed twice with strong nitric acid, and the plug is returned to the beaker in which the precipitation was made. The filtering tube is washed with water and hydrochloric acid to dissolve any adhering precipitate; 25 cc. strong hydrochloric acid are added and 1 or 2 cc. dilute sulphuric acid in order to precipitate any

barium that may be present.[1] The solution is heated to boiling with constant stirring to avoid bumping, and when all the manganese dioxide is dissolved, the suspended asbesos is removed by filtration. The solution, made up to a half liter, is treated with ammonia until a very slight permanent precipitate of ferric hydroxide forms, 10 or 15 cc. of a 25 per cent. solution of ammonium acetate are added, and the solution is heated to boiling and boiled for a few minutes. Filter into a half-liter flask with the aid of suction and wash the flask and funnel once with hot water. The precipitate is dissolved in dilute hydrochloric acid into the same flask in which the precipitation was made and a second basic acetate precipitation carried out as before. Filter into the flask containing the filtrate from the first basic acetate precipitate and wash the flask and precipitate twice with hot water. The subsequent precipitation can be made in the flask, or the united filtrates may be transferred to a No. 6 beaker, and 10 cc. acetic acid added. The solution is heated to boiling, 10 or 15 grams of ammonium phosphate crystals are added, and the solution stirred until the precipitate of ammonium manganese phosphate begins to assume the well-known crystalline form; 25 cc. of strong ammonia are now slowly added and the solution stirred for a few minutes and set aside for subsidence of the precipitate which should have a decidedly crystalline appearance. Filter through an 11 cm. filter by aid of suction and wash with hot water; burn, and weigh as $Mn_2P_2O_7$. 38.74 per cent. of the weight is manganese.

When a single analysis only is required, 1 gram may be weighed off and treated as directed for 5 grams.

The fusion of the insoluble residue of the ore is important as a silicate of manganese may occur, not distinguishable by its color from pure silica after ignition in the crucible

Determination of Silica in Pig Iron

Twice the factor weight (0.9404 gram) of the drillings is weighed off, placed into a 12 cm. porcelain dish, and 25 cc. of sili-

[1] At this stage of the analysis, if barium occurs in the ore, which is usually the case, the nitrate, being very insoluble in strong nitric acid, will be wholly or partially precipitated. Consequently it will be filtered off with the manganese dioxide, and will ultimately go into solution in the subsequent dilution, and boiling with hydrochloric acid. The barium must be separated by sulphuric acid and sufficient time must be allowed for its precipitation.

con mixture are added. The dish is heated over an Argand burner until all is dissolved and afterwards until dense fumes of sulphuric acid are given off. After cooling add sufficient dilute hydrochloric acid (1 part hydrochloric acid, 2 parts water). Dilute with hot water and warm until all is dissolved but the separated silica and carbon. Filter, wash with hot water and hydrochloric acid until free from iron, burn, and weigh. One-half the weight in decimilligrams represents hundredths per cent. silicon.

The silicon mixture is made by mixing 18 cc. of nitric acid (sp. gr. 1.20) and 7 cc. of sulphuric acid (sp. gr. 1.38).

Determination of Sulphur in Pig Iron and Steel

GRAVIMETRIC METHOD

Five grams of pig iron or steel are weighed off and placed into a No. 5 beaker with a watch-glass cover, and 50 cc. aqua regia added at once. (The aqua regia is prepared by mixing 45 cc. strong nitric acid and 5 cc. strong hydrochloric acid and is always used directly after its preparation.) When the violent action has ceased, heat is applied until all is dissolved. Evaporate, the beaker being covered, until the fluid is considerably reduced in bulk. About 40 cc. strong hydrochloric acid are then added and the solution, after continued evaporation, is transferred to a 12 cm. porcelain dish and allowed to go to dryness on a steam-bath. Thirty-five cc. strong hydrochloric acid are then added and the solution evaporated until ferric chloride begins to separate in a solid state as indicated by a film floating on the surface. This is dissolved by the addition of a drop or two of strong hydrochloric acid and the solution is diluted to 75 cc. Filter into a No. 2 beaker, washing with hot water and hydrochloric acid just sufficient to dissolve the last trace of iron. Heat nearly to boiling and add 10 cc. of a 5 per cent. barium chloride solution. The solution is again evaporated until a film of ferric chloride appears. Dissolve by addition of a drop or two of strong hydrochloric acid, and with a wash-bottle a strong stream of cold water is forced into the solution until its volume is about 175 cc. It is then set aside in a cool place over night. Filter, using a double 7 cm. filter, and wash with hot water and dilute hydrochloric acid until free from iron. Burn in an open crucible and weigh. 13.756 per cent. of the weight of the barium sulphate is sulphur.

EVOLUTION METHOD

Five grams of pig iron or steel are weighed off into a dry half-liter flask, provided with a doubly perforated rubber stopper, carrying a long-stem funnel tube and a delivery tube bent at a right angle, upon the end of which a short piece of rubber hose is placed, making connection with a tube also bent at a right angle reaching to the bottom of a test-tube 2.5 cm. wide and 25 cm. deep. About 10 cc. of the ammoniacal solution of cadmium chloride are introduced into the test-tube which is then filled to two-thirds its depth with cold water. Eighty cc. of dilute hydrochloric acid (1 volume of acid, 2 volumes of water) are then poured into the funnel tube and gentle heat applied until the iron is all dissolved. Finally heat to boiling and maintain at the boiling-point until nothing but steam escapes from the delivery tube.

The apparatus is then disconnected and the delivery tube is placed into the No. 4 beaker in which the titrations are made. The contents of the test-tube are poured into the beaker and the test-tube rinsed by filling twice with cold water. Its sides are washed with 25 cc. dilute hydrochloric acid and it is once more rinsed by filling with water. The acid and water are supplied from overhead aspirator bottles and suitable rubber tube connections with pinch-cocks. The total volume of the solution and washings should be about 400 cc. Five cc. of starch solution are then added.

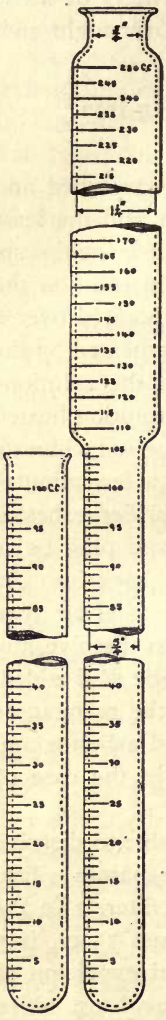
Without waiting for complete solution of the cadmium sulphide, the iodine solution is run in from a burette, stirring gently, till a blue color is obtained; the solution is then stirred vigorously, keeping a blue color by fresh additions of the iodine solution, and more till the precipitate of cadmium sulphide is all dissolved, and the proper permanent blue color is obtained. The amount of iodine solution used in cubic centimeters is hundredths per cent. sulphur.

SOLUTIONS

Iodine Solution.—Weigh off into a dry 500 cc. flask, about 35 grams potassium iodide, and 16 grams iodine. Add 50 cc. of water, shake, and dilute cautiously until all is in solution, and finally dilute to 3.5 liters. This is standardized with steels of known sulphur content, so that 1 cc. equals 0.0005 gram sulphur.

COLOR METHOD FOR MANGANESE IN PIG IRON AND STEEL

Two-tenths gram each of pig iron or steel and of standard steel of known manganese content, are weighed off into 1 x 10 inch test-tubes. Add 30 cc. of nitric acid (sp. gr. 1.20) to both portions, heat till dissolved, and boil till all the nitrous fumes are driven off. While boiling, about one gram of lead peroxide is added and the boiling continued for two minutes; the test-tubes are placed into the cold water-bath to cool and allow subsidence of the excess of lead peroxide. When cool, and the supernatant liquid is clear, the tube containing the standard solution is decanted into one of the comparing tubes; this can be very safely done without losing more than a drop of the solution, and without a particle of the lead peroxide entering the tube. The solution is then diluted to twice the number of cubic centimeters that the steel contains hundredths per cent. manganese, and mixed thoroughly. The test, pig iron or steel, is decanted in like manner into the other comparing tube, and diluted with cold water to like colors. One-half the reading in cubic centimeters is hundredths per cent. manganese.



COMPARISON TUBES FOR COLORIMETRIC MANGANESE DETERMINATIONS.

In case the manganese is high in the sample (0.75 per cent. or more) one-half the above quantity, or 0.1 gram, is taken. The method of procedure is the same. The comparison tubes used are represented in the accompanying drawing. The color tubes used show plainly their advantages over the ordinary tubes.

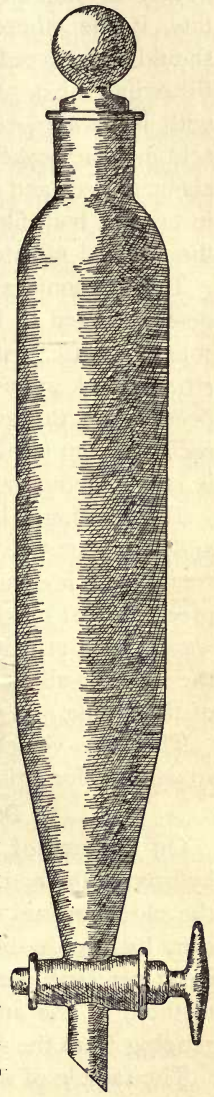
Determination of Nickel in Steel

ETHER METHOD

In the determination of nickel the ether method for the separation of nickel from iron has in this laboratory supplanted the acetate method formerly in use. The details are as follows:

In a 12 cm. porcelain dish with a watch-glass cover dissolve 2

grams of the sample in a 30 cc. of strong hydrochloric acid. When in solution add 3 cc. nitric acid (sp. gr. 1.20), evaporate by hard boiling while still covered, until the bulk of the solution is reduced to about 10 cc. Allow to cool and wash the solution into the separatory tube (shown in the cut) with the least possible amount of hydrochloric acid (sp. gr. 1.13).



It is important to keep the solution as concentrated as possible. Now pour cautiously down the side of the separatory tube 45 cc. of ether (free from alcohol), insert the stopper (firmly holding in place with the thumb), place under a stream of water from a tap, and shake vigorously from one to two minutes; then place in the rack and allow to stand a few minutes until the two liquids separate completely. Remove the stopper and draw off the acid solution slowly into a No. 4 beaker; this can be done to the last drop by bringing the ethereal solution containing the iron just to the stop-cock. Now pour into the tube 5 cc. of the hydrochloric acid (sp. gr. 1.13), insert the stopper, shake, allow to separate, and drain off as before into the main solution, this time bringing the ethereal solution just through the stop-cock.

This washing of the ethereal solution is usually neglected in every-day practice as the separation of the two liquids can be made so completely that the loss of nickel is very trifling. The objection to the washing is that it largely increases the iron content of the acid solution. In case the washing is neglected the acid solution is drawn down until the ethereal solution just passes through the stop-cock and one drop taken of the ethereal solution. Rinse off the end of the tube into the beaker, place the beaker over a lamp, and boil for about five minutes to drive off the dissolved ether; dilute with hot water to 200 to 225 cc. and add ammo-

nia until just alkaline, then 10 cc. strong ammonia in excess, heat to boiling, and boil a few minutes. The iron in this precipitate, if the ethereal separation has been properly carried out, should not exceed 1.5 per cent. of the weight originally taken. Filter into a No. 5 beaker and wash the beaker and precipitate once with hot water, redissolve the precipitate in dilute hydrochloric acid into the beaker in which the precipitation was made, dilute to about 125 cc., and reprecipitate the iron with ammonia, using 5 cc. in excess; boil, filter, and wash into the No. 5 beaker containing the original filtrate.

The ammoniacal filtrate containing all the nickel and manganese is heated to boiling and hydrogen sulphide passed into the solution until it smells strongly of the gas, or 15 to 20 cc. of strong stock ammonium sulphide added, or 30 to 40 drops (depending on the amount of nickel present) of thiacetic acid, in each case, but particularly in the latter, being sure that the solution is still ammoniacal.

The solution is boiled gently for a few minutes, acetic acid then added (about 5 cc. in excess of the neutral point), and the boiling continued a few minutes longer. Remove from the heat, allow the precipitate of nickel sulphide to subside and filter, wash with hot water, burn at a low temperature until the paper is charred and the sulphide all converted into oxide, and finally in the hottest part of the muffle. Weigh as NiO.

The glass vessel represented in the sketch on p. 45 has proved convenient for agitation of the solution with ether.

Determination of Carbon in Steel

On account of the economy of time effected by the barium hydroxide method, it has, in this laboratory, entirely superceded the older method of absorption of the carbon dioxide in potassium hydroxide solution and weighing. The results agree within 0.003 per cent. with those obtained repeatedly in using the older method, in the analysis of great numbers of samples of metal ranging from the softest up to the hardest spring steel.

The sample of steel (from 1 to 10 grams) is placed in a beaker and 100 to 500 cc. of a solution of the double chloride of potassium and copper are added. This solution is prepared by dissolving 5 pounds of the double salt in 5 liters of water, filtering

through a plug of purified asbestos and adding 250 cc. of strong hydrochloric acid. The beaker is placed upon a suitably arranged stirring apparatus, in which the stirrers make about 250 revolutions per minute, and kept at a temperature of about 50° C. until the metal is dissolved. It is best to allow time for cooling of the solution and the subsidence of the separated carbon. The solution is then filtered through a perforated platinum boat with a suitable asbestos blanket, and washed once with dilute hydrochloric acid, and then with warm water, allowing all the washings to run from the beaker into the boat. The boat is then dried at 85° C. and is finally transferred to the combustion tube. The accompanying photograph shows the arrangement of the combustion apparatus. In front of the combustion furnace is the double purifying train for oxygen and air. The first bottles, A and A′, contain a strong solution of potassium hydroxide (sp. gr. 1.4). The jars, B and B′, are filled with stick potash in short pieces. These purifiers are connected by means of a three-way tube, with suitably arranged stop-cocks and rubber tubing, with the platinum combustion tube resting in a 10-burner furnace. The tube is of 15.6 mm. inside diameter and 425 mm. long, and provided with a gas-tight joint, and prolongations 150 mm. long and 8.4 mm. internal diameter. Five cm. from the rear end of the tube is placed a coil of platinum gauze 5 cm. long completely filling the tube, then a layer of coarse copper oxide 5 cm. long, and then another coil of platinum gauze. Connected with the combustion tube is a 10-bulb absorption tube. The apparatus being ready a stream of oxygen, flowing at the rate of 4 bubbles per second, is turned on. 100 cc. of a solution of barium hydroxide (containing 20 grams to the liter) are introduced by means of a pipette into the absorption tube taking care not to touch its interior surface with the pipette. The absorption tube is now connected, by means of a soft rubber stopper and a short piece of rubber hose, with the combustion tube.

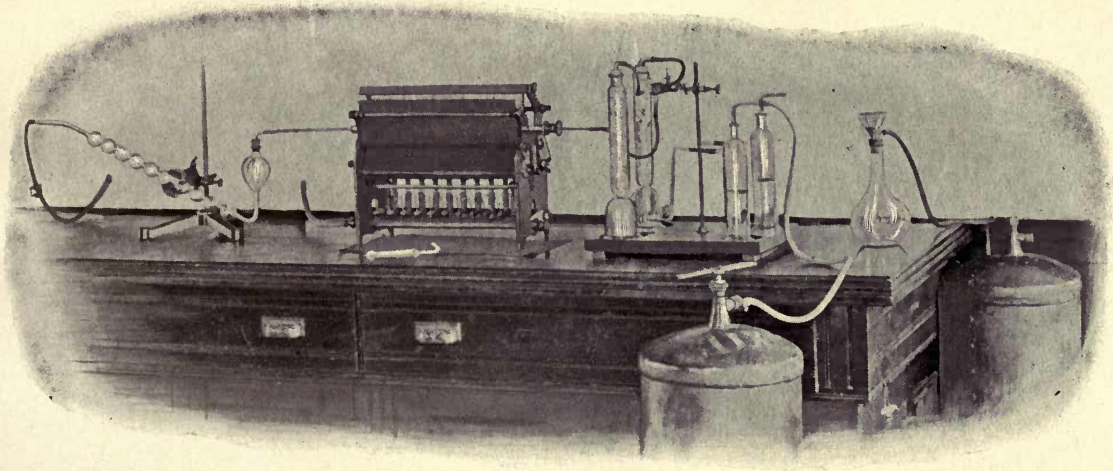
The burners under the platinum gauze and copper oxide are ignited, and after the tube has been brought to full redness the burners in front of the boat are turned on, and finally those under it until the tube is at a bright red heat throughout. The oxygen stream is then continued for ten minutes longer, after which it is shut off. Purified air is aspirated through the train

by means of the rubber tubing shown connected to the end of the absorption tube, which up to the time has been disconnected, and which is now slipped onto the tube maintaining the same rate of flow of four bubbles per second for ten minutes longer.

Continuing the aspiration, the stopper is now removed from the end of the absorption tube, thus holding the solution in place and preventing its flowing back into the bulb of the absorption tube and carrying the precipitate with it; the thumb is then placed on the opening, the aspirator tube slipped off and the tube shaken to loosen any adhering precipitate of barium carbonate and then held vertically over a suction flask, the funnel of which is provided with a platinum cone and a tightly fitting 11 cm. filter. Moderate suction is applied so that with the funnel full of water and a full stream in the stem no air is drawn between the paper and the funnel. Now by loosening the thumb pressure all the solution is allowed to flow into the funnel in a gentle stream carrying the bulk of the precipitate with it. Let the funnel drain and wash the absorption tube repeatedly till free from the precipitate, with water that has previously been boiled to free it from carbonic acid and cooled slightly, taking care not to breathe into the wash-bottle, and finally the precipitate is washed three or four times from another wash-bottle in the ordinary manner.

The precipitate is burned in a platinum crucible and weighed as barium carbonate containing 6.09 per cent. of carbon.

In the meantime, during the washing of the tube and precipitate, the platinum tube has been cooled sufficiently for the removal of the boat and the insertion of another, the weighing of the precipitate being done during the aspiration for the next combustion. The time required for a determination is about thirty minutes.



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VIII. Method Used at the Laboratory of the Shenango Valley Steel Co., New Castle, Pa.

By A. L. Cromlish

Determination of Silica and Iron in Ores

Weigh 1 gram of the sample into a No. 2 beaker, add 25 cc. of strong hydrochloric acid, cover with a watch-glass, and digest at a temperature just short of boiling until the ore is decomposed; dilute with 25 cc. of water and filter into a No. 4 beaker. The residue is then burned and fused with sodium carbonate, the fusion dissolved in the filtrate from the residue, and the whole allowed to go to hard dryness. Redissolve the mass in about 15 cc. of strong hydrochloric acid, dilute, filter into a 300 cc. flask, and wash the residue 3 or 4 times with hot water, ignite, and weigh as SiO_2. In the filtrate the iron is deoxidized by granulated zinc and determined by titration with a standard bichromate solution; the addition of the standard is continued until a drop of the iron solution added to a drop of potassium ferricyanide solution no longer produces a blue coloration on standing one-half minute. The number of cubic centimeters of bichromate solution used multiplied by 100 times the value of 1 cc. in iron gives the percentage of iron.

Potassium Bichromate Solution.—Dissolve 17.570 grams of the fused salt in water, dilute to 2 liters and standardize with iron wire.

Determination of Phosphorus in Ores

Digest 5 grams of the sample, dried at 100° C., in a No. 2 beaker covered with a watch-glass, in 50 cc. of strong hydrochloric acid. When the ore appears to be perfectly decomposed, dilute, and filter into a No. 5 beaker. The residue is burned and fused with sodium carbonate, the fusion dissolved in hot water, the solution acidified with strong hydrochloric acid and added to the

original filtrate; the combined solutions are allowed to go to hard dryness on the hot plate. The mass is then moistened with a little hydrochloric acid, diluted with a sufficient amount of water to dissolve the sodium salt, and filtered into a 400 cc. Erlenmeyer flask. The process is then carried on as in case of steel.

Determination of Manganese in Iron Ores

Two grams of the sample are dissolved and further treated in the same manner as for phosphorus and the solution filtered into a 500 cc. flask. The solution is neutralized with ammonia until a slight permanent precipitate forms. Redissolve this with a few drops of hydrochloric acid, and add ammonium carbonate, drop by drop, until a faint precipitate is formed. Add about 4 grams of sodium acetate, boil one minute, and allow the precipitate to settle. Filter into a 500 cc. flask, and wash two or three times with hot water. The precipitate is washed back into the same flask in which the precipitation was made, and dissolved in the least possible quantity of hydrochloric acid. The precipitation is repeated exactly as before. Unite the filtrates and proceed as in the case of steel.

Determination of Silicon in Pig Iron

Twice the factor weight (0.9340 gram of the drillings) is weighed off into a No. 5 beaker. Add 50 cc. of water, and then pour 20 cc. of sulphuric acid (sp. gr. 1.85) into the mixture, directing the acid to the center of the beaker. Evaporate until copious fumes of sulphuric acid are given off. Cool the beaker over a cold blast jet. Add 100 cc. of water and 4 or 5 cc. of hydrochloric acid. Boil until all iron sulphate has dissolved, filter hot, wash at first with dilute hydrochloric acid (1 part acid, 1 part water), and then with hot water; ignite and weigh. One-half the weight in decimilligrams is the percentage of silicon in hundredths.

Determination of Sulphur in Iron and Steel

GRAVIMETRIC METHOD

Dissolve 5 grams of the drillings in a No. 5 beaker, covered with a watch-glass, in 50 cc. of strong nitric acid. When the violent action has ceased, add 15 cc. of strong hydrochloric acid, and, when solution is complete, about one-half gram of sodium carbonate, and evaporate the solution to hard dryness. Remove the

beaker from the heat; when cold add 40 cc. of strong hydrochloric acid, and heat, gently at first, until the iron oxide is dissolved; evaporate again to a sirup, and, if any ferric chloride separates, add a few drops of strong hydrochloric acid; dilute and filter, washing with the least possible amount of dilute hydrochloric acid to remove the last trace of iron. Heat the filtrate, which should have a volume of about 400 cc., to boiling, add 5 cc. of a saturated solution of barium chloride, and allow to stand at about 40° C. over night. Filter through a 9 cm. Munktell's No. 1 filter; wash with a little dilute hydrochloric acid (1 part acid, 1 part water), and finally with hot water; dry, ignite, and weigh as $BaSO_4$.

EVOLUTION METHOD

Place 3 grams of the drillings into a dry 500 cc. flask provided with a doubly perforated rubber stopper; the stopper carries a one-bulb thistle tube, and a small piece of glass tubing bent at right angles; the latter is connected by a short piece of rubber tubing to a glass tube running to the bottom of an intervening bottle; the exit tube of the bottle is connected by rubber tubing to a delivery tube, also bent at right angles, reaching to the bottom of a 1 x 8 inch specimen tube, which is connected by rubber stopper and delivery tube with a second specimen tube. The whole apparatus is suitably supported. Dilute 15 cc. of an ammoniacal cadmium chloride solution to 100 cc. with cold water, and pour one-half into each of the specimen tubes. About 100 cc. of boiling water are added to the 500 cc. flask, and the flask connected with the apparatus above described. Introduce, through the thistle tube, 50 cc. of strong hydrochloric acid. When the sample has dissolved, boil the solution until the steam reaches the first specimen tube, then disconnect at the latter, turn out the light, and allow the flask to draw back the acid and water which has distilled into the intervening bottle. Transfer the contents of the specimen tubes to a 400 cc. Erlenmeyer flask, rinsing the tubes with a little hydrochloric acid and water. Now add a few cubic centimeters of starch solution, acidulate with strong hydrochloric acid, and immediately run in the iodine solution, from a burette, agitating the contents of the flask at the same time until the proper blue color is

obtained. The volume, in cubic centimeters, of iodine solution used multiplied by the value of 1 cc., is the percentage of sulphur in the sample.

Cadmium Chloride Solution.—Dissolve 120 grams of cadmium chloride in 1500 cc. of water and add 600 cc. of strong ammonia.

Iodine Solution.—Weigh out into a half-liter flask 8 grams of iodine and 20 grams of potassium iodide. Add about 100 cc. of water. Allow to stand over night and dilute to 2 liters. The solution is standardized with an iron of known sulphur content. The known percentage of sulphur divided by the number of cubic centimeters of solution required is the strength of the iodine solution.

Determination of Phosphorus in Pig Iron and Steel

Three grams of drillings are dissolved in a No. 5 beaker in 40 cc. of nitric acid (sp. gr. 1.20) and the solution evaporated to hard dryness. Allow the beaker to cool, dissolve the precipitate in 30 cc. of strong hydrochloric acid, dilute with cold water, filter into a 400 cc. Erlenmeyer flask and wash the filter with cold water. Add 10 cc. of strong ammonia and agitate the mixture until the precipitate formed is all dissolved. The solution is heated or cooled to 60° C., and 50 cc. of molybdate solution are added by aid of a pipette; the flask is shaken for two or three minutes and then allowed to stand until the precipitate has settled. Filter, collect the precipitate on a 7 cm. S. & S. No. 589 filter, and wash with dilute molybdate solution (water containing 5 per cent. by volume of the stock solution). Pour 3 or 4 cc. ammonia on the precipitate, stir it up with a fine jet of water and allow the solution to run into the flask in which the precipitation was made. Add, drop by drop, enough strong hydrochloric acid to cause the separation of the yellow precipitate, and then ammonia until it redissolves. Pour the solution back through the filter, allowing it to run into a 120 cc. Erlenmeyer flask, and wash two or three times with cold water. To the cold solution add very slowly 10 cc. of magnesia mixture, agitating constantly, and, after the precipitant is all in, 5 cc. of strong ammonia. Shake vigorously. Stand the flask in cold water for about one hour, filter through a 7 cm. S. & S. No. 589 paper, and wash with 5 per cent. ammonia. Ignite over the blast-lamp at a low heat, and weigh as $Mg_2P_2O_7$.

Molybdate Solution.—Dissolve 100 grams of molybdic acid in

450 cc. of strong ammonia. Pour 1250 cc. nitric acid (sp. gr. 1.20) into a 2,500 cc. bottle, and place the bottle into a pail of cold water. Now add, in small portions, the molybdic acid and ammonia, taking about thirty minutes for the operation. The mixture is kept in a warm place for forty-eight hours and is then ready for use.

Magnesia Mixture.—Dissolve 280 grams of ammonium chloride together with 110 grams of magnesium chloride in 1,300 cc. water, and add 700 cc. of strong ammonia. Allow the preparation to stand four or five days before using.

Determination of Manganese in Steel in Pig Iron

Dissolve 3 grams of the drillings in a No. 5 beaker in 50 cc. nitric acid (sp. gr. 1.20), evaporate until the solution is almost of a sirupy consistence, add 100 cc. of strong nitric acid, heat the solution to boiling, and while boiling add 5 grams of potassium chlorate in small portions. Continue the boiling for ten minutes. Cool the solution rapidly by standing the beaker in a pan of cold water; filter by aid of a pump through purified asbestos supported by a small piece of pumice stone in the stem of the filtering tube; wash two or three times with strong nitric acid. Transfer the precipitate, with the asbestos filter, to the beaker in which the precipitation was made. The filtering tube is washed off with water and a little hydrochloric acid; add about 5 cc. of strong hydrochloric acid and agitate the contents of the beaker until the asbestos is all suspended. Heat the mixture till the precipitate is dissolved, filter from the asbestos into a No. 2 beaker, and wash with hot water. To the filtrate add enough ammonium acetate to precipitate the last traces of iron, boil, and filter into a 400 cc. Erlenmeyer flask.

Determination of Manganese in Steel

One-tenth of a gram of each sample and of the standard is measured off into 1-inch by 8-inch test-tubes. Pour into each test-tube 15 cc. of nitric acid (sp. gr. 1.20). When the violent action has ceased boil over an Argand burner till nitrous fumes are driven off. While boiling, add about five-tenths of a gram of lead peroxide, and boil each sample and the standard exactly one minute. The tubes thus filled are immediately placed in cold water and set aside in a dark place. When cool, and the

excess of peroxide has settled out, leaving the supernatant liquid perfectly clear, the standard solution is decanted into one of the comparing tubes. The solution is then diluted with water to as many cubic centimeters as the standard contains hundredths of 1 per cent. of manganese, and mixed thoroughly with the water. The test sample is decanted in the same manner, and diluted with cold water until it has the same shade as the standard solution. The reading in cubic centimeters represents the percentage of manganese in hundredths.

Determination of Manganese in Pig Iron

It is preferable in this case to dissolve 1 gram. To the filtrate add an excess of strong ammonia, and then, with a vigorous shake, a few cubic centimeters of bromine. Heat gradually to boiling, allow the precipitate to settle, filter, and wash with cold water. The washing of the precipitate is easily accomplished by means of cold water, there being no fixed alkali present. Ignite over a blast-lamp at a low temperature and weigh as Mn_3O_4.

Or, in the case of pig iron, dissolve in 50 cc. of dilute hydrochloric acid. Dilute, and filter into a No. 5 beaker, evaporate down to nearly a sirup, being careful not to heat too hot. Redissolve in 50 cc. of strong nitric acid, and evaporate to total expulsion of hydrochloric acid. Add 100 cc. of strong nitric acid, heat to boiling, add 5 grams of potassium chlorate, and proceed as described for steel.

Determination of Nickel in Steel

Dissolve 1 gram of the drillings in a No. 4 beaker in 25 cc. of nitric acid (sp. gr. 1.20) and evaporate to hard dryness. Redissolve in 15 cc. of strong hydrochloric acid and separate the iron exactly as directed in the "Determination of Manganese in Ores." Unite the filtrates and boil down until their volume is reduced to about 300 cc. Acidulate with a few drops of acetic acid, heat to boiling, and pass hydrogen sulphide till the solution smells strongly of the gas. Boil a few minutes until the precipitate has a flocculent appearance. Filter and wash with hot water, ignite the filter and precipitate, and transfer them to a No. 2 beaker. Dissolve in 3 or 4 cc. of strong hydrochloric acid with a few drops of strong nitric acid, evaporate to dryness, redissolve in a few drops of strong hydrochloric acid, dilute to about 100 cc., heat to

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boiling and pass hydrogen sulphide through the solution; allow the precipitate to subside, filter if necessary, wash with hot water, and if desired burn and weigh as Cu_2S. Add an excess of ammonia to the filtrate, pass hydrogen sulphide, allow the precipitate to subside, filter, wash, ignite in a porcelain crucible, and weigh as NiO.

IX. Methods Used at the Laboratory of the Clinton Iron and Steel Company, Pittsburg, Pa.

By A. B. Harrison

Determination of Iron in Iron Ores

Weigh out two samples of 0.5 gram each of the finely ground and dried ore, and brush into Erlenmeyer flasks of 500 cc. capacity. Add 25 to 30 cc. of concentrated hydrochloric acid, insert into the neck of each flask a rubber stopper with a glass tube of 3 mm. bore, and 35 cm. long.

One end of the glass tube should extend 12 mm. below the stopper. Place the stoppered flasks on the edge of a hot plate and allow to digest till all soluble matter is in solution. The residue on shaking the flask should appear floating and light, and free from dark heavy particles. This may take from fifteen to twenty minutes or longer, and may be hastened by adding a few crystals of potassium chlorate, in which case the solution must be heated until free from chlorine. Cool and dilute with its own volume of water. Reduce with 5 cc. of stannous chloride solution; usually 5 cc. are sufficient to reduce the ferric to ferrous chloride, but, in case the solution still manifests the ferric chloride color, add a drop or two more of the stannous chloride solution until the ferric chloride is all reduced. Dilute to 300 cc. with water, and precipitate the excess of stannous chloride with mercuric chloride. Titrate now with standard solution of potassium bichromate, using potassium ferricyanide as an indicator. Note the number of cubic centimeters of bichromate used and calculate the percentage of iron.

Reactions.—A strongly acid solution of ferric chloride if boiling hot is almost instantly reduced to ferrous chloride by a solution of stannous chloride, the end of the reaction being judged by the disappearance of the yellow color due to ferric chloride.

The excess of stannous chloride is removed by mercuric chloride which is reduced to insoluble mercurous chloride, the latter being without action on the iron or bichromate, the stannous chloride being converted into stannous chloride. This reaction is satisfac-

tory provided that not too much stannous chloride is present, and that the mercuric chloride is in large excess, and the solution not too hot; otherwise metallic mercury may be formed as a gray precipitate which will act on the bichromate and cause false results.

The solution of ferricyanide used as an indicator must be made up fresh daily, a piece the size of a pea being dissolved in 100 cc. of water.

Standardize the bichromate solution against pure iron wire and C. P. ferrous ammonium sulphate crystals. Dissolve 4.39 grams of the fused salt in 1 liter of water.

For the stannous chloride solution dissolve 100 grams of the salt in 100 cc. of concentrated hydrochloric acid and add 300 cc. of water. Boil with some scraps of tin till clear and colorless, and then bottle. A saturated solution of mercuric chloride is used, keeping some of the salt in the bottle.

One cc. of the bichromate solution of above strength equals 0.005 gram Fe; on an 0.5 gram sample, 1 cc. equals 1 per cent. Fe.

Determination of Silica in Ores

Treat 1 gram of the ore with 25 cc. concentrated hydrochloric acid in a covered 10 cm. round-bottomed evaporating dish. Evaporate to dryness and heat till the residue is dry and scaly. Cool and redissolve with 15 cc. of concentrated hydrochloric acid and evaporate to dryness again, cool and take up with concentrated hydrochloric acid, warm till all iron is in solution, dilute with water, filter through a 12½ cm. filter, and wash free from iron salts and acid; dry, burn, and weigh as silicious residue. This may consist of free silica, silicates, titanium oxide, barium sulphate, etc. It is better always to fuse this residue with sodium carbonate to separate the silica. Or the residue may be treated with hydrofluoric acid and the silica obtained by difference. In the latter case add to the weighed silica, etc., in the crucible, 1 to 10 cc. of hydrofluoric acid and 10 cc. of sulphuric acid, and evaporate to dryness over a low flame; heat to bright redness, cool, and weigh. The difference is silica.

Determination of Alumina, Lime and Magnesia in Iron Ores

When the amount of manganese is low in the ore proceed as in

the method given under limestone; when the amount of manganese is over 1 per cent. proceed as directed in Blair's "Chemical Analysis of Iron," third edition, p. 238.

Determination of Phosphorus in Ores

Weigh, of Bessemer ores, 5 grams, of other ores 2 to 3 grams, into a 10 cm. evaporating dish, and dissolve in 70 cc. of concentrated hydrochloric acid, evaporate to dryness on a hot plate, heat till the residue no longer smells of acid, cool, and take up with 50 cc. concentrated hydrochloric acid and boil till all but the silicious residue is in solution. Dilute with 50 cc. water and filter through a quick filter. Wash with hot dilute hydrochloric acid and hot water alternately till free from iron, burn the residue and paper, and fuse with sodium carbonate. Take up the fusion with boiling water, dissolve any particles adhering to the crucible with dilute hydrochloric acid, and acidulate the solution of the fusion with hydrochloric acid. Evaporate to dryness, bake, cool, and take up with dilute hydrochloric acid. Boil, filter off silica, receiving the filtrate in the beaker containing the original filtrate from the solution of the ore. Wash the silica on a filter which may be burned and the silica determined if necessary.

To the filtrates, evaporated to as small a volume as possible (about 20 cc.), add 50 cc. nitric acid (sp. gr. 1.42). Evaporate to 20 cc., cool and neutralize with ammonia and proced as in the analysis of pig iron.

Molybdate Solution.—Wood's formula (1888).

One pound of molybdic acid is suspended in 1200 cc. of water and 700 cc. of strong ammonia added. After all soluble matter is in solution 300 cc. of strong nitric acid are added. In each of 4 2-liter bottles put 1200 cc. of water and 500 cc. of strong nitric acid. When solutions are cool, add to each of the 4 bottles 550 cc. of the solution of molybdic acid, pouring through a funnel and giving a circular motion to the solutions. Allow to stand several days and filter before using.

In the case of limestones, clays, etc., proceed as in the analysis of ores.

Determination of Sulphur in Iron Ores

Weigh out 5 grams into a No. 4 evaporating dish, suspend in a few cubic centimeters of water, and add a few drops of bromine, 45 cc. of strong nitric acid, and 10 cc. of strong hydrochloric

acid. Digest on the hot plate until all soluble matter is in solution. Evaporate to 10 cc. or until sirupy, add a pinch of sodium carbonate, and evaporate to dryness. Cool, redissolve in 50 cc. of strong hydrochloric acid, boil, dilute with 30 cc. of water, and filter; wash free from iron, etc., burn the residue and fuse with sodium carbonate. Dissolve the fusion in water, or as much of it as is possible, acidulate with dilute hydrochloric acid and evaporate to dryness in the evaporating dish used for the first solution of the ore.

Take up with dilute hydrochloric acid, filter, receiving filtrate and washings in the beaker containing the first solution of the ore. Wash free from iron salts (and chlorides if it is desired to determine the silica), evaporate the combined filtrates to a small volume (about 30 cc.), and add 10 cc. of a 10 per cent. solution of barium chloride. Dilute to 60 cc. with hot water; add 1 or 2 cc. of concentrated hydrochloric acid if necessary, and allow to stand covered with a watch-glass on the edge of a hot plate till the precipitate has settled. Filter through an ashless filter, burn and weigh. Calculate the weight of barium sulphate to sulphur. With ores containing large amounts of sulphides it is better to fuse the ore with sodium carbonate and sodium nitrate, and separate from the silica as above and determine the sulphur in the filtrate as $BaSO_4$.

Determination of Manganese in Iron Ores

See Volhard's method as given under Analysis of Pig Iron.

Determination of Silicon in Pig Iron

Weigh out 0.4702 gram of drillings into a 5½ inch flat-bottomed evaporating dish and dissolve in 30 cc. of silicon mixture. After all effervescence has subsided, heat over a low flame until all is in solution, keeping a watch-glass cover over the dish, and evaporate to dryness (till dense white fumes of sulphuric acid appear). Then cool and moisten with dilute hydrochloric acid, wash off cover with hot dilute hydrochloric acid, dilute the contents of dish with water to 100 cc. and boil till all iron salts are in solution. Filter, wash the residue of silica and graphite with hot water and hot dilute hydrochloric acid alternately till free from iron; finally wash with water till free from acid. Burn and weigh the silica remaining. The weight multiplied by 100 gives the percentage of silicon in the sample. In mill irons use twice

the factor weight and divide by 2 and multiply by 100 to determine the percentage.

Silicon Mixture.—Mix together 1500 cc. of water, 500 cc. of nitric acid (sp. gr. 1.42), and 150 cc. of sulphuric acid (sp.gr.1.82).

Determination of Sulphur in Pig Iron and Steel

EVOLUTION METHOD

The amount as indicated by the strength of the iodine solution is weighed out and brushed into a half-liter flat-bottomed flask with a side delivery tube bent at a right angle. In a 350 cc. beaker put 50 cc. of the cadmium chloride solution and dilute to two-thirds full with water. Set the beaker on a small piece of asbestos board on the edge of a hot plate. Insert the rubber stopper and thistle-tube into the neck of the flask so that the end of the tube is close to the bottom of the flask; then place the flask so that the end of the delivery tube of the flask almost touches the bottom of the beaker.

Then through the thistle-tube add to the flask 150 cc. of hydrochloric acid (1:1), and allow to dissolve slowly; when all the iron is in solution bring to boiling. Disconnect by lifting the flask away from the beaker.

To the contents of the beaker when cold add 2 or 3 cc. of starch solution and 15 cc. strong hydrochloric acid, and, while stirring, add iodine solution from a burette, slowly, and stir gently till a blue color is obtained. The contents of the beaker are then stirred vigorously, keeping a blue color by fresh additions of iodine solution till the precipitate is all dissolved, and a permanent blue color is obtained. The amount of iodine solution used in cubic centimeters represents hundredths per cent. of sulphur.

Cadmium Chloride Solution.—100 grams of cadmium chloride are dissolved in 1 liter of water; add 500 cc. of strong ammonia, filter if necessary, and dilute with water to 2 liters. Then make up to 4 liters with strong ammonia. For use, dilute 100 cc. of this solution with 1500 cc. of water and 500 cc. of strong ammonia.

Iodine Solution.—4 grams of resublimed iodine and 6 grams of potassium iodide are dissolved in 10 cc. of water, and when all is dissolved dilute with water to 2 liters.

Starch Solution.—Suspend 4 grams of starch in 50 cc. of water and add to 2 liters of boiling water; boil for several minutes, stirring constantly; cool, and add 100 cc. of normal sodium hydroxide solution. Use the clear solution.

Standardizing the Iodine Solution.—Weigh out 7.75 grams of sodium hyposulphite and dissolve in a liter of water. Weigh out 2.46 grams of fused potassium bichromate and dissolve in 500 cc. of water. One cc. of this solution will set free 0.0127 gram of iodine from a solution of potassium iodide in dilute hydrochloric acid.

Reaction.—$K_2Cr_2O_7 + 6KI + 14KCl = 8KCl + Cr_2Cl_6 + 7H_2O + 6I$. 1 cc. of the $K_2Cr_2O_7$ solution contains 0.00492 gram of the salt, $294.5 : 761.1 :: 0.00492 : x$. $x = 0.1271$ gram iodine.

From a burette add 20 cc. of bichromate solution to a solution of 1 gram of potassium iodide in 100 cc. of water and 15 cc. of dilute hydrochloric acid in a 350 cc. beaker. This sets free 0.2540 gram of iodine.

From a burette add hyposulphite solution to this definite amount of iodine till a greenish color appears; then add starch solution and continue titrating till the blue color disappears. Allow to stand exactly seven minutes and if a blue color becomes manifest, add a drop or two more of hyposulphite solution. The reaction is considered complete when upon standing for seven minutes no further blue color becomes apparent. The amount of hyposulphite solution used is divided into the amount of iodine set free in the potassium iodide solution (0.2540 gram), and this gives the value of 1 cc. of hyposulphite solution in terms of iodine.

Now take 20 cc. of the iodine solution, dilute to 100 cc. and titrate with the hyposulphite solution till the blue color from the addition of starch disappears.

The number of cubic centimeters of hyposulphite solution used multiplied by the value of 1 cc. in iodine, gives the value of the 20 cc. of iodine solution in terms of iodine. Divide by 20 to get value per cubic centimeter. Multiply this value (in terms of iodine) by 32.06 and divide by 253.9 to get the value in terms of sulphur per cubic centimeter.

Example.—One cc. of bichromate liberates 0.0127 gram iodine; 20 cc. of bichromate liberates 0.2540 gram; this amount of iodine

required 63.9 cc. of hyposulphite to discharge the blue color; 1 cc. of hyposulphite equals 0.003975 gram iodine.

Twenty cc. of iodine solution took 9.8 cc. of hyposulphite (0.038955 gram iodine).

One cc. of iodine solution equals 0.00194775 gram iodine.

One cc. of iodine solution equals 0.000247 gram sulphur.

Therefore using 2.47 grams of drillings, 1 cc. of iodine solution equals 0.01 per cent. sulphur.

GRAVIMETRIC METHOD

The method commonly known as the aqua regia method is used to check results. Weigh out 2 to 5 grams of drillings and brush them into a No. 4 evaporating dish. Carefully add 25 to 40 cc. concentrated nitric acid, cooling the dish if the action is too strong, or heating if too slow. When nearly all is in solution, carefully add 5 to 10 cc. concentrated hydrochloric acid, and slowly bring to boiling. Cover with a watch-glass and continue the evaporation on a hot plate or sand-bath. When the solution is sirupy add a pinch of sodium carbonate and continue the evaporation to dryness. Bake slightly, cool, and moisten with hydrochloric acid and evaporate again to dryness. Cool and take up with 30 cc. of strong hydrochloric acid. Heat till all iron salts are in solution and the volume is about 15 cc. Dilute with an equal volume of water, filter and wash the residue free from iron, using hot dilute hydrochloric acid and hot water, alternately, receiving the filtrate and washings in a 250 cc. beaker. The filtrate should not exceed 75 cc. Heat and add 5 to 10 cc. of a 10 per cent. solution of barium chloride; allow to stand on the edge of the hot plate till the liquid becomes clear. Filter through a small ashless paper, washing out iron, etc., with hot water and dilute hydrochloric acid. Wash several times, till free from acid, with water alone. Dry, ignite, and weigh as barium sulphate, containing 0.137 part sulphur.

Determination of Phosphorus in Pig Iron and Steel

3.26 grams of pig iron (in case of steel 5 grams are used) are dissolved in 60 cc. of nitric acid (sp. gr. 1.2) in a 15 cm. evaporating dish with a watch-glass cover. Evaporate to dryness, still covered, and heat over the flame uncovered till all acid fumes are driven off and the residue curls from the dish. When

cool dissolve in 30 cc. of strong hydrochloric acid and evaporate to a small volume (till the excess of free acid is driven off, as indicated by the appearance of insoluble ferric chloride on the bottom of the dish). This is dissolved by adding 20 to 30 cc. of strong nitric acid. Boil till free from nitrous fumes, and the volume of the liquid is about 10 to 15 cc. Filter into a half-liter Erlenmeyer flask; wash the dish and paper with 5 per cent. nitric acid, neutralize with ammonia, bring back to a clear amber color with strong nitric acid, heat or cool to 85° C., add 80 cc. of molybdate solution, and whirl or shake for several minutes. Allow to settle and filter through a weighed paper which has been dried between watch-glasses in the air-bath at 110° C. for fifteen minutes and cooled in a desiccator.

Wash with 2 per cent. nitric acid, heat in the air-bath at 110° C. for an hour or until dry, cool in a desiccator, and weigh.

The yellow precipitate contains 1.63 per cent. phosphorus. See Blair's "Analysis of Iron," third edition, page 92, *et seq.*

MAGNESIA METHOD FOR PHOSPHORUS

This is used to check the results obtained by weighing the yellow precipitate. The two methods are identical up to the filtering off of the yellow precipitate, when the use of a weighed filter is omitted. Wash free from iron, etc., using 5 per cent. nitric acid, dissolve the yellow precipitate from the paper with ammonia water (1:4), wash the paper with water, and neutralize the filtrate with a drop or two of hydrochloric acid. Add a drop of bromine, make ammoniacal, set on the edge of a hot plate, and heat just to boiling; if silica separates out, filter off on a small ashless washed paper and wash with water. Add a drop or two of a 10 per cent. solution of citric acid to the clear filtrate and cool. Then stir in 10 cc. of the magnesia mixture; add 10 cc. of ammonia (sp. gr. 0.96) and allow to stand in a cool place, or in ice-water, for not less than six hours. Filter through a 9 cm. No. 590 Schleicher and Schuell filter-paper, taking care to detach any of the precipitate adhering to the sides of the beaker. Wash with 10 per cent. ammonia water, burn, and weigh. Then add to the crucible and contents 5 cc. of nitric acid (sp. gr. 1.20) and allow to simmer for a minute or two on the edge of the hot plate. Then refilter through a 9 cm. No. 590 Schleicher and

Schuell filter-paper, wash the beaker with as little water as possible, and wash the paper once with cold water. Burn and weigh. The difference between the weights is the weight of magnesium pyrophosphate, containing 0.2790 part of phosphorus.

Determination of Manganese in Pig Iron

COLOR METHOD

Weigh out 0.2 gram each of standard and of sample into test-tubes 1 inch by 10 inches, and dissolve with 30 cc. nitric acid (sp. gr. 1.13). Bring to boiling, and when free from nitrous fumes cool by placing the test-tubes into cold water. Add about 10 grams of lead peroxide to each test-tube, washing down with a jet of water any particles adhering to the sides. Heat again and boil for two minutes. Cool and allow to settle, then carefully decant off the clear liquid into comparing tubes and compare. Calculation: number of cubic centimeters of standard: number of cubic centimeters of sample: : per cent. of manganese in standard: x; x equals percentage manganese in sample. For spiegel and ferromanganese use the "Acetate Method" as given in Blair's "Chemical Analysis of Iron," third edition, page 109, *et seq.*

VOLHARD'S METHOD

See Blair's "Chemical Analysis of Iron," page 118, *et seq.*

Weigh out 1 gram of drillings and dissolve in 30 cc. of silicon mixture in a 14 cm. flat-bottomed evaporating dish.

After effervescence is over, add 3 cc. of hydrochloric acid, cover the dish with a watch-glass and evaporte to dryness, cool, and take up with water, and boil till all iron salts are in solution. Transfer to a liter flask, dilute to 300 cc., bring to boiling, and add zinc oxide cream. Titrate, while boiling hot, with potassium permanganate, without filtering off the precipitate. In case of ores dissolve in concentrated hydrochloric acid and filter off the insoluble residue, which should be fused to recover any manganese insoluble in hydrochloric acid. Combine the filtrates (from the first solution and from the silica of fusion), evaporate to dryness with silicon mixture, and proceed as in the analysis of pig iron.

Determination of Graphitic Carbon in Pig Iron

EGGERTZ' METHOD MODIFIED

In an 8 ounce beaker dissolve 1 gram of drillings in 100 cc. of dilute hydrochloric acid, when the sample is white iron or iron high in combined carbon; in case of foundry or Bessemer iron, dissolve in 100 cc. of nitric acid (sp. gr. 1.20). When dissolved add a drop or two of hydrofluoric acid and boil until all nitrous fumes are driven off; filter through tared papers.

Place the papers into separate funnels, filter through the paper on the left, wash out the beaker with a little water, detaching any adhering particles with a rubber-tipped glass rod. Then pass the filtrate through the paper on the right. Wash each paper several times with water alone, then wash out iron salts with hot dilute hydrochloric acid and hot water, alternately; wash free from acid, then wash each paper with 5 per cent. ammonia. Wash repeatedly with ammonia till free from any soluble organic matters; *i. e.*, till washings are colorless. Wash free from ammonia, then once with a mixture of alcohol and ether (equal parts), dry at 96° C., cool, and weigh. The difference in weight between the papers is the weight of silica, graphite, etc. Burn the paper containing the graphitic residue, and weigh its ash. Subtract this ash from the weight of graphitic residue and the difference is graphite.

By tared papers is meant two papers that have been dried in an air-bath for fifteen minutes at 96° C., and have been carefully cut to equal weight. The washing with ammonia is necessary to remove organic compounds which have come down with the graphitic residue. The ether-alcohol wash removes traces still remaining, and helps to dehydrate, and thus shorten drying in the air-bath.

Instead of using tared papers a Gooch crucible can be used and the time materially shortened. With a Gooch crucible use disks of filter-paper, drying the crucible and disk in the air-bath and taking the weight of the crucible and filter. Filter and wash as directed in the above method; dry the crucible and contents, weigh, and then ignite the residue and subtract the ash as before.

Determination of Combined Carbon in Pig Iron

The color method is used as in the analysis of steel, filtering

off the graphitic residue, and passing the standard through same sized filter.

Determination of Manganese in Steel

Volhard's method is used as given under Analysis of Pig Iron. The potassium chlorate method is also used to check the results, dissolving the precipitate of manganese dioxide with standard ferrous sulphate solution, and titrating the excess of ferrous sulphate solution. See Lord's "Notes on Metallurgical Analysis," page 44.

Determination of Carbon in Steel.

The color method is used as given in Blair's "Chemical Analysis of Iron," second edition, page 161, *et seq.*

Determination of Nickel in Steel.

The method of Blair is used as described in "Chemical Analysis of Iron," third edition, p. 184.

X. Methods Used at the Laboratory of the W. Dewees Wood Company, McKeesport, Pa.

By R. B. Carnahan, Jr.

Iron Ores

The sample, which has been put through a 100 mesh sieve, is dried thoroughly at 100° C. just previous to analysis.

Determination of Silica in Iron Ores

Fuse 1 gram of the ore with 5 grams sodium carbonate and 0.25 gram potassium nitrate in a platinum crucible. Acidify with hydrochloric acid and evaporate to dryness. Redissolve in sufficient water and hydrochloric acid, filter, wash with dilute hydrochloric acid (sp. gr. 1.1) and hot water, burn, and weigh. Treat the ignited residue in the usual way with hydrofluoric acid and a few drops of sulphuric acid; the loss in weight represents the quantity of silica in the ore.

Determination of Iron in Ores

Dissolve 0.75 gram of the sample in concentrated hydrochloric acid, heating on the steam-bath over night. Deoxidize the ferric iron of the solution with stannous chloride, adding the latter gradually. When the solution is entirely colorless, cool somewhat, and then add 10 cc. of mercuric chloride solution. Titrate in the regular way with standard potassium bichromate, using a very dilute solution of potassium ferricyanide to determine the end reaction.

Solutions.—The mercuric chloride is a saturated aqueous solution. The stannous chloride solution contains 150 grams of the salt dissolved in 1 liter of hydrochloric acid (sp. gr. 1.1). To prepare the standard bichromate, dissolve 7 grams of the salt in 1 liter of water, and dilute so that 1 cc. is equivalent to 0.0075 gram of iron. The solution is standardized from a steel of known composition.

Determination of Phosphorus in Ores

From 3 to 5 grams of ore (according to the percentage of phosphorus) are dissolved in strong hydrochloric acid, and the solu-

tion is evaporated to dryness; the residue is redissolved in a few cubic centimeters of strong hydrochloric acid and water, and the silicious matter remaining filtered off and ignited. The latter is fused with a little sodium carbonate, the fusion dissolved in nitric acid and water, and the nitric solution added to the original filtrate, which is again evaporated to dryness. After dissolving in a little hydrochloric acid and water, the silica is removed by filtration. The filtrate is made slightly alkaline with ammonia, and then slightly acidified with nitric acid. The solution, which measures about 125 cc., is heated to 80° C.; 50 cc. of molybdate solution are added, and it is left to stand for about ten minutes. The yellow precipitate is filtered by the aid of suction and washed with pure water. It is then titrated with standard alkali, the solution being standardized by steels and pig irons in which the phosphorus has already been determined by the molybdate-magnesia method, according to Blair's "Analysis of Iron," 1896 edition.

SOLUTIONS

The molybdate solution is made by dissolving 1 pound of molybdic acid in 1 liter of strong ammonia and 1 liter of water, and pouring this solution into 6.5 liters of nitric acid (sp. gr. 1.2).

Determination of Manganese in Ores

From 3 to 5 grams of ore are dissolved in strong hydrochloric acid, and the solution evaporated to dryness. The dry mass is redissolved in hydrochloric acid and water, and the insoluble residue filtered off and ignited. The residue is fused with sodium carbonate, and the fusion dissolved in hydrochloric acid and water. The solution, after separating the silica, is added to the main solution; potassium chlorate is then added, care being taken to expel the chlorine generated in excess. The iron is precipitated as basic acetate, the precipitate being redissolved and reprecipitated twice. For each gram of ore 2 grams of ammonium acetate are used. The combined filtrates are then concentrated and the manganese precipitated by bromine as dioxide. The precipitate is filtered off and dissolved in hydrochloric acid, the solution neutralized with ammonia, and the manganese again precipitated as ammonium manganese phosphate, according to Blair. Ignite and weigh as $Mn_2P_2O_7$. When the percentage of manganese is less than 0.5, the manganese dioxide is converted for weighing into protosesquioxide.

Determination of Silicon in Pig Iron

Dissolve 1 gram of borings in 10 cc. of "silicon mixture" and 25 cc. water. Evaporate until the formation of fumes of sulphuric acid begins. When sufficiently cool, dissolve in a little water and about 10 cc. of strong hydrochloric acid. Filter, using suction, wash with hot water and dilute hydrochloric acid (sp. gr. 1.10), ignite and weigh as silica.

SOLUTIONS

The "silicon mixture" is made by addig 200 cc. of strong sulphuric acid to 800 cc. of strong nitric acid.

Determination of Sulphur in Pig Iron

Weigh 5 grams of the drillings into a 500 cc. flask, add 50 cc. of water, and, after connecting the flask with the absorption apparatus, add 50 cc. of strong hydrochloric acid. Without delay light a small flame under the flask, and dissolve as rapidly as desired. The evolved gas bubbles through 50 cc. of ammoniacal cadmium chloride solution contained in a 7-inch foot test-tube. When the drillings have dissolved, boil the solution to expel the last traces of hydrogen sulphide from the flask. Rinse out the contents of the test-tube into a shallow porcelain dish, make slightly acid with hydrochloric acid, add starch solution, and titrate to a decided blue color with a standard iodine solution.

SOLUTIONS

Ammoniacal cadmium chloride solution is made by dissolving 30 grams of cadmium choride in 5 liters of water and 1 liter of strong ammonia. The iodine solution is prepared by dissolving 8.5 grams of iodine and about 25 grams of potassium iodide in a small quantity of water, and diluting to 2 liters. This solution is then exactly standardized by a standard steel (rather high in sulphur) in which the percentage of sulphur has been exactly determined by the aqua regia method, as described by Blair in the third edition of his "Chemical Analysis of Iron." Except only in a very few cases, all pig irons are tested for sulphur by the evolution method.

Determination of Phosphorus in Pig Iron

Dissolve 3 grams of the sample in 50 cc. of nitric acid (sp. gr. 1.20), evaporate to dryness, and heat the residue over a bare flame for five minutes. Cool, dissolve in a few cubic centimeters

of strong hydrochloric acid, and evaporate until the solution measures about 10 cc. Then add about 20 cc. of strong nitric acid, and boil for about four minutes. Dilute with water and filter. The solution should have a volume of about 75 cc. Complete the determination as in the case of ores.

For the sake of rapidity we use the following method for several grades of Bessemer pig iron: Dissolve 3 grams of the metal in 100 cc. of nitric acid (sp. gr. 1.13). When the borings have completely dissolved add a saturated solution of potassium permanganate till a decided precipitate remains. Boil three minutes and then add 10 cc. of strong hydrochloric acid. Filter off the carbonaceous residue and proceed further as described for ores.

Determination of Manganese in Pig Iron

Dissolve 3 to 5 grams of the sample in 50 cc. of nitric acid (sp. gr. 1.20), evaporate to dryness, and ignite for five minutes. Cool, redissolve in a few cubic centimeters of hydrochloric acid, evaporate the excess of acid, and filter. Make the basic acetate separation, etc., as described under Iron Ores.

The color method is also used largely for pig irons; *viz.*, dissolve 0.5 gram of pig iron in 15 cc. of nitric acid (sp. gr. 1.20) in an 8-inch test-tube, filter, and dilute the filtrate to 50 cc. Draw off 10 cc. with a pipette and place the solution in an 8-inch test-tube. Add 3 cc. of nitric acid (sp. gr. 1.20). Heat to boiling, add about 2 grams of lead peroxide, and boil the mixture for two minutes. Add about 15 cc. of cold water, and allow the tube to stand in cold water till the lead peroxide settles completely. Compare the color of the sample for analysis with that of a standard pig iron treated similarly. Standards are always made by the basic acetate method, the manganese being weighed as pyrophosphate.

Determination of Sulphur in Steel

See Pig Iron.

Determination of Phosphorus in Steel

See Pig Iron.

The permanganate oxidation method is generally used; the filtering off of silica becomes unnecessary in this case.

Determination of Carbon in Steel

Dissolve 3 grams of steel in 200 cc. of a saturated solution of

cupric potassium chloride, containing 10 cc. of strong hydrochloric acid, at 60° C., with constant stirring.

Filter off the carbonaceous residue on an asbestos plug, and wash with dilute hydrochloric acid and hot water.

Transfer the residue to a 500 cc. flask and burn with a mixture of chromic and sulphuric acids, absorbing for weighing the carbon dioxide evolved.

The combustion train is as follows:

1. A 500 cc. flask.
2. An empty tube.
3. A tube containing 0.2 gram of pyrogallic acid, 5 grams of potassium oxalate, 3 grams of sodium chloride, 0.2 gram of sulphuric acid, and water necessary to make the volume 20 cc.
4. A tube containing silver sulphate and strong sulphuric acid.
5. A tube containing sulphuric acid.
6. An empty tube.
7. Geissler potash bulbs containing caustic potash (sp. gr. 1.27); and a guard U-tube containing strong sulphuric acid.

After the combustion, pure air is aspirated through the apparatus for twenty minutes.

Blanks are made, and the apparatus frequently checked by steels of known carbon content. The various minute details are carried out about as given in Blair's work above quoted.

Determination of Manganese in Steel

See Pig Iron.

The silica filtration is not generally necessary, however.

Determination of Nickel in Steel

Make the basic acetate separation, using 1 gram of steel, and to the filtrate add 10 grams of ammonium acetate and 6 drops of acetic acid. Precipitate with hydrogen sulphide, filter, burn and weigh as NiO (and CuO, should copper be present).

Dissolve the ignited precipitate in hydrochloric acid and a few drops of nitric acid, dilute with water and precipitate any copper in the solution with hydrogen sulphide.

Burn, and weigh as CuO; subtract the weight of the CuO from the first weight. The difference represents the quantity of NiO derived from the sample.

XI. Methods Used at the Laboratory of the Republic Iron and Steel Company, Youngstown, Ohio

By H. L. Brinker

Determination of Silica in Ores

Weigh 5 grams of ore, which has been dried at 100° C. for one hour, into a 12 cm. porcelain dish, add 75 cc. concentrated hydrochloric acid, and boil for one-half hour. Remove from the heat, dilute with hot water and filter into another dish of the same size, wash with dilute hydrochloric acid (3 parts acid, 5 parts water) and hot water. Place on a sand-bath and evaporate to dryness. Take up with 25 cc. concentrated hydrochloric acid and evaporate until it becomes sticky, dilute with hot water, and filter into a 500 cc. graduated flask. The original residue is placed in a platinum crucible, cautiously burned, cooled, and fused with sodium carbonate. The fused mass is dissolved in hot water, made acid with hydrochloric acid, and evaporated to dryness. Take up with a few cubic centimeters of dilute hydrochloric acid (3 parts acid, 5 parts water) and hot water, and, when solution is complete, filter through the same filter into the 500 cc. graduated flask in which the original solution is contained. The combined residues are now washed with as small a quantity as possible of dilute hydrochloric acid, and then with hot water until free from chlorine. Burn in a platinum crucible, and weigh as silica.

Determination of Iron in Ores

The filtrate from the silica in the 500 cc. flask is diluted to the mark with water at the temperature of the room, 100 cc. are taken out with a 100 cc. pipette with which the flask has been accurately calibrated, and placed into a 500 cc. flask fitted with a rubber stopper having a Bunsen valve. Add 50 cc. of dilute sulphuric acid (1:4) and 15 grams of zinc. Keep the flask cool and when all action has ceased apply heat, but do not boil. Cool, pour into a No. 5 beaker into which 50 cc. dilute sulphuric acid (1:4) have

been placed, and wash the flask well, decanting from the residue of zinc. Make the beaker about two-thirds full and titrate with standard solution of potassium permanganate, making an allowance for a blank determination on the zinc which is carried along side by side with the ore analyses, and use the same weight of zinc in both cases. In the presence of titanium reduce with hydrogen sulphide, expel the hydrogen sulphide and titrate.

Determination of Phosphorus in Ores

Treat 5 grams of the ore with 75 cc. strong hydrochloric acid as in the case of the determination of silica and iron, and evaporate to dryness. The residue is taken up with 25 cc. strong hydrochloric acid, and evaporated until the solution becomes sticky and the iron salt is on the point of separating out. Five cc. concentrated nitric acid are then added and the solution shaken to dissolve any iron salt that may be separated. Dilute to a small bulk and filter into a half-liter flask. The fused residue is treated with a few drops of dilute nitric acid (sp. gr. 1.20) and hot water, and poured into the filter through which the original solution had been filtered. The combined residues are washed once with water, once with a 2 per cent. nitric acid solution, and twice with hot water. The residue can be removed to another flask and well washed with hydrochloric acid and water, burned and weighed as a check on the silica determination. To the filtrate add 25 cc. strong ammonia and then 25 cc. strong nitric acid, which should just redissolve the precipitate and leave the solution slightly acid. Heat to exactly 85° C. and add 75 cc. ammonium molybdate solution, shake for five minutes, and allow to stand for half an hour. Filter through a 9 cm. Munktell filter, which has been dried at 110° C. for one hour and ten minutes and weighed between ground watch-glasses at once after removal from the oven. The yellow precipitate is washed with a 2 per cent. nitric acid solution, the excess of water removed by means of a blotter, and the filter dried at 110° C. for one hour and ten minutes, and weighed between watch-glasses. If arsenic or titanium is present the method of Blair ("Chemical Analysis of Iron," third edition, p. 81) is followed.

The Ammonium Molybdate Solution is made by dissolving 200 grams of molybdenum trioxide in 500 cc. water with 500 cc. am-

monia and adding this solution slowly, with constant shaking, to 2500 cc. dilute nitric acid (sp. gr. 1.20); keep in a warm place for twenty-four hours, before using.

Determination of Manganese in Ores

Weigh 5 grams of ore into a 12 cm. dish, add 75 cc. concentrated hydrochloric acid, boil for about one-half hour, filter into another 12 cm. dish, and evaporate to dryness. Take up with 25 cc. concentrated hydrochloric acid and evaporate to a small bulk. Remove from the heat and add 5 cc. strong nitric acid (sp. gr. 1.42), and shake the dish to bring all the iron salt into solution; dilute with hot water and filter into a No. 4 beaker. Place the original residue into a platinum crucible, burn, fuse with sodium carbonate, and dissolve the fusion in hot water acidulated with hydrochloric acid, and evaporate to dryness. Take up with a few cubic centimeters of dilute nitric acid (sp. gr. 1.20) and hot water, and pour through the same filter and into the No. 4 beaker containing the original filtrate; wash once with 2 per cent. nitric acid and hot water. The combined filtrates are then evaporated twice with concentrated nitric acid to the sticking point, 100 cc. nitric acid (sp. gr. 1.42) added, and the solution brought to the boiling-point. The manganese dioxide is then precipitated by potassium chlorate and the solution boiled for a few minutes. Remove from the lamp, and cool. Filter through an asbestos filter and wash once with colorless strong nitric acid. When dry, transfer the asbestos and precipitate to the original beaker and wash the filtering tube with strong hydrochloric acid and water, using in all about 20 cc. acid. Heat with constant shaking over a lamp until the manganese dioxide is entirely dissolved. Filter off the asbestos, receiving the solution in a half-liter flask. Wash well and make a basic acetate precipitation. Filter into a No. 6 beaker. Redissolve this precipitate in hydrochloric acid and repeat the basic acetate precipitation, filtering into the original solution. Make the solution in the beaker acid with acetic acid, and heat to boiling; precipitate manganese with ammonium phosphate, boil the precipitate until crystalline (stirring if necessary), add 25 cc. strong ammonia, and boil for a few minutes longer. Remove from the heat and allow to settle, filter, and wash with hot water about five times, being

careful not to stir up the precipitate on the paper. Absorb the moisture with a blotter and burn in a porcelain crucible until white. Use the necessary precautions for barium and lead.

Determination of Silicon in Pig Iron

Weigh 0.9404 gram of iron, dissolve in 25 cc. of a mixture of 28 parts of nitric acid (sp. gr. 1.20) and 12 parts of dilute sulphuric acid (1 part acid, 1 part water). As soon as solution is complete, evaporate to dryness; when dry, raise the heat until copious fumes of sulphuric acid escape. Cool, add a few cubic centimeters of dilute hydrochloric acid (3 parts acid, 5 parts water) and 25 cc. hot water, warm until solution is complete, filter and wash once with water, once with dilute hydrochloric acid (3 parts acid, 5 parts water) and four times with hot water. Absorb the excess of water on a blotter. Place into a crucible, burn, cool and weigh, and divide by 2. The result is per cent. of silicon.

Determination of Sulphur in Pig Iron and Steel

EVOLUTION METHOD

Place 5 grams of the metal into a half-liter flask, provided with a doubly perforated stopper, carrying a separatory funnel of cylindrical form and an exit tube for gas which is connected with a tube extending to the bottom of a test-tube 2.5 cm. deep and 25 cm. long. This test-tube contains 10 cc. of cadmium chloride solution, to which sufficient water is added to fill the tube about two-thirds full. The cadmium chloride solution is made by dissolving 100 grams of the salt in 500 cc. water, filtering into a 2 gallon bottle and adding water to make up 3 liters; then add 8 liters ammonia. To the drillings contained in a flask add 80 cc. dilute hydrochloric acid (3 parts acid, 5 parts water), place over an Argand burner and warm, lower the flame until solution is complete, then increase the heat again until steam drives all gas from the flask. Disconnect the flask and pour the solution with the yellow sulphide from the test-tube into a No. 4 beaker. Wash out with water and enough dilute hydrochloric acid (3 parts acid, 5 parts water) to dissolve the sulphide and make the solution acid. Titrate immediately with iodine solution which has been standardized with a sulphur standard to read the percentage. Each 0.1 cc. = 0.001 per cent. sulphur. The beaker should be

two-thirds full of cold water, and while titrating be sure that all sulphide is dissolved.

AQUA REGIA METHOD

Weigh 5 grams of drillings into a No. 4 beaker, add a mixture of 5 cc. strong hydrochloric acid and 40 cc. strong nitric acid to the drillings at once. Heat until the solution is complete, add 40 cc. strong hydrochloric acid, transfer to a 12 cm. dish, and evaporate to hard dryness. Cool, add 30 cc. strong hydrochloric acid and evaporate to the formation of a crust; add a few drops of hydrochloric acid, dilute and filter into a No. 2 beaker, wash well, and fill the beaker about two-thirds full of water; heat to boiling and add 5 cc. barium chloride solution (25 grams in 500 cc. water). Allow to stand over night on the sand-bath, then evaporate to formation of a crust, add a few drops of hydrochloric acid and fill half full with water, and again evaporate until a crust forms; add a few drops of hydrochloric acid, fill two-thirds full of cold water, and allow to stand over night at the temperature of the room. Filter through a double filter (No. 590, 7 cm. wide), wash well with hydrochloric acid and water, burn, and weigh. If necessary purify this precipitate.

Determination of Phosphorus in Pig Iron and Steel

Dissolve 5 grams of the drillings in a 12 cm. dish, using 60 cc. nitric acid (sp. gr. 1.20) in case of steel, and 75 cc. in case of pig iron. When the solution is complete (which will be the case in a few minutes if the metal is a steel, and about three-fourths hour if a pig iron), evaporate over an Argand burner at a strong heat, using a watch-glass cover. When near dryness reduce the heat and be sure that any iron salt, which may have splashed upon the glass, is dissolved and carried down into the dish. As soon as dry, remove the watch-glass and heat over a lamp until all acid fumes are gone. Cool and add for a steel 30 cc. and for a pig iron 35 cc. strong hydrochloric acid, replace the watch-glass, and place over a low flame until solution is complete. Then evaporate as rapidly as possible until the solution becomes viscid. Remove from the lamp and add 5 cc. strong nitric acid and a few cubic centimeters of water, and shake the dish to bring any iron salt, which may have separated, into solution. Wash the watch-glass with hot water and continue to dilute until the volume of the solution amounts

to about 100 cc. Filter into a half-liter flask, washing paper and residue with a 2 per cent. solution of nitric acid and hot water. Proceed as in the case of the determination of phosphorus in ores.

Determination of Manganese in Iron and Steel

COLOR METHOD

Weigh 0.2 gram iron or steel, place into a test-tube 2.5 cm. wide and 25 cm. deep, and add 25 cc. nitric acid (sp. gr. 1.20); when solution is complete and all nitrous fumes are gone, add about 0.5 gram lead peroxide and boil for two minutes, cool in water, and when settled compare the color with that of a standard which has been treated in exactly the same way, the manganese in the standard having been determined gravimetrically. Dilute the standard to twice as many cubic centimeters as the percentage of manganese and divide the number of cubic centimeters of all compared with it by 2. It takes some time for the solution of pig iron, and the solution should be kept over a very low flame so as not to reduce its bulk before adding the lead peroxide.

GRAVIMETRIC METHOD

Dissolve 5 grams of steel in 60 cc. nitric acid (sp. gr. 1.20), and evaporate to a pasty condition in a No. 4 beaker. Add 100 cc. strong nitric acid and heat to boiling. Precipitate the manganese dioxide with potassium chlorate. Filter through asbestos and proceed as with manganese dioxide in ores. Pig iron is treated in the same way as for the determination of phosphorus until it is filtered into a half-liter flask. For manganese it is filtered into a No. 4 beaker and evaporated twice with 40 cc. nitric acid (sp. gr. 1.40) to a pasty condition. 100 cc. strong nitric acid are added and the solution is brought to the boiling-point. The manganese is then precipitated by potassium chlorate. Proceed then as in the case of the determination of manganese in steel and in iron ores.

Determination of Carbon by Combustion

The steel or iron is dissolved in a solution of the double chloride of copper and potassium. This solution is made by dissolving 5 pounds of the salt in 6 liters of water, filtering through asbestos and adding 5 per cent. of hydrochloric acid. For 3 grams of steel 180 cc. of this solution are used. If a stirring machine is not used, stir well and allow to stand over night at the tempera-

ture of the room. Then warm on a sand-bath, stirring frequently until all copper is in solution, cool, and filter through ignited asbestos in a funnel as described by P. W. Shimer.[1] The carbon is well washed with hydrochloric acid and water until free from hydrochloric acid and copper. The felt is placed on a watch-glass and dried at 90° C. for an hour. The dried felt is placed, carbon side down, into the bottom of a platinum crucible of a Shimer combustion apparatus and heated (for steel twenty minutes and for pig irons thirty minutes) over a blast-lamp. Air is forced through the apparatus by the flow of distilled water from one aspirator bottle into another. Immediately following this bottle is a potash bulb filled with a solution of potash of 1.40 specific gravity; then comes the crucible and water-cooled stopper and following this the brass tube filled with copper oxide and heated over a Bunsen burner. Following the brass tube is a tube filled with glass beads moistened with water and kept cool by a wet wick applied externally; then a sulphuric acid bulb or U-tube partly filled with sulphuric acid. Following these are the absorption bulbs (Geissler's potash with drying tube), which are filled with potash solution of about 1.40 specific gravity. The drying tube is filled with calcium chloride. Connected with this is a Liebig bulb filled with sulphuric acid to serve as a trap. Then comes a calcium chloride tube, used as a protection but not weighed. A blank is always run before each day's work and must not yield more than 0.0005 gram carbon. Where a number of combustions are to be made the Geissler and Liebig bulbs are weighed and then placed in the train for the next combustion, using the weight from the last one in beginning the next following, until the day's work is completed. Test the joints each time the apparatus is put together.

Determination of Silicon in Steel

Dissolve 5 grams of the sample in 50 cc. nitric acid (sp. gr. 1.20) and add 35 cc. dilute sulphuric acid (1:1). Evaporate in a 12 cm. dish, using a watch-glass cover until bumping begins, remove the glass, and stir until the solution becomes solid. Heat until copious fumes of sulphuric acid are given off. Cool, add about 20 cc. dilute hydrochloric acid and 100 cc. water, heat until the solution is complete, and filter and wash well with hydrochloric acid and water; burn and weigh.

[1] *J. Am. Chem. Soc.*, **21**, 557 (1899).

XII. Methods Used at the Laboratory of the Isabella Furnace Co., Etna, Pa.

By F. G. Brinker

Determination of Silica in Iron Ores

Dissolve 1 gram of the finely powdered ore in hydrochloric acid, dilute, filter, wash, and fuse the residue with a mixture of sodium and potassium carbonates. The fusion is dissolved in a beaker in hydrochloric acid. Evaporate to dryness and bake. Dissolve in hydrochloric acid, dilute the solution, filter, wash the residue with hot water and dilute hydrochloric acid, and again with hot water. Burn and weigh.

Determination of Iron in Iron Ores

Dissolve 1 gram of the ore, finely pulverized, in a flask in 40 cc. hydrochloric acid, at a gentle heat. Add 1 gram of potassium chlorate. Place a funnel into the neck of the flask and boil gently until chlorine is expelled. Dilute to 50 cc., heat nearly to boiling, and deoxidize with a solution of stannous chloride measured by means of a burette. Cool, and titrate back the excess of stannous chloride with a solution of iodine.

If greater accuracy be required filter and fuse the insoluble residue, dissolve in acid and add to the main solution before deoxidizing.

In preparing the standard iron solution, I use fine iron wire and treat it as above described. The first factor is found by standardizing the stannous chloride and iodine solutions. Take 2 cc. of stannous chloride solution, dilute, add a little starch solution, and titrate with iodine solution. Divide the number of cubic centimeters of iodine into the number of cubic centimeters of stannous chloride. Multiply the number of cubic centimeters of iodine used to titrate back the excess of stannous chloride used by this factor, and subtract from the total volume of stannous chloride used for the reduction. The second factor is found by

dividing the number of cubic centimeters of stannous chloride, used for the standard after the excess has been subtracted, into the weight of pure iron in the iron taken.

Multiply the number of cubic centimeters of stannous chloride solution by this and by 100. This gives the percentage of iron in the sample.

SOLUTIONS USED

Stannous Chloride Solution.—Dissolve 60 grams of the crystals in 125 cc. hydrochloric acid and 125 cc. water. To this solution there are added 650 cc. hydrochloric acid and 1650 cc. water.

Iodine Solution.—This contains 8 grams iodine dissolved in potassium iodide solution and diluted to 1 liter.

The permanganate method, as described in Blair's "Chemical Analysis of Iron," second edition, is also used, deoxidizing by zinc. When titanium is present, use acid ammonium sulphate.

Determination of Manganese in Iron Ores and Pig Iron

Williams' method is used and also Volhard's method, as described in Blair's "Chemical Analysis of Iron," second edition.

Determination of Phosphorus in Iron Ore

The molybdate-magnesia method is used, as described by Blair.

Determination of Silicon in Pig Iron

Dissolve 0.9333 gram of the drillings in a casserole in hydrochloric acid, and evaporate to dryness. Cool and take up with hydrochloric acid, heating the mixture to boiling. Dilute, filter, wash with dilute hydrochloric acid, and finally with hot water. Ignite cautiously until the filter has been burned off. The ignition is then continued for fifteen minutes at the highest heat of a gas blast-lamp; cool and weigh. The weight of the silica found, divided by 2 and multiplied by 100, gives the percentage of silicon.

Determination of Phosphorus in Pig Iron

Weigh 1.63 grams of well-mixed borings into a 500 cc. beaker, and add cautiously 35 cc. nitric acid (sp. gr. 1.20). Boil down to dryness and bake on a hot plate at 200° C. for thirty minutes. Redissolve in hydrochloric acid, add 35 cc. of concentrated nitric acid, and evaporate until the volume of the solution is reduced to about 15 cc. Remove from the hot plate, dilute with hot water,

filter, and to the filtrate add ammonia until a precipitate forms which does not disappear on stirring. The neutralized solution is treated with 3 cc. of concentrated nitric acid, which should suffice to redissolve the precipitate and give a clear, amber-colored liquid, not red in tint. The solution is then heated to about 70° C., the molybdate solution added, and the mixture shaken for five minutes. Allow the precipitate to settle, collect it on a weighed filter, and wash with water containing 2 per cent. of nitric acid. Dry in the air-bath at 120° C. for thirty minutes after all visible moisture has disappeared, and weigh.

XIII. Methods Used at the Laboratory of the Cambria Steel Co., Johnstown, Pa.

By F. S. Hyde

Determination of Silica in Ores

Dissolve 1 gram of the dried ore in strong hydrochloric acid. Evaporate to dryness, moisten with hydrochloric acid, add water, boil, and filter, washing with hot dilute hydrochloric acid and hot water; burn the filter and fuse the ash, silica, and insoluble matter with sodium carbonate. Remove the fusion to a porcelain dish with water and acid; render acid with strong hydrochloric acid and evaporate to dryness and finally bake.

Cool, moisten with hydrochloric acid, add water, boil and filter, washing with hot dilute hydrochloric acid and water. Burn the filter in a platinum crucible; cool and weigh; add a few drops of water, and 3 drops each of strong sulphuric and hydrofluoric acids. Evaporate, burn, and weigh the crucible again. The loss in weight is silica.

Determination of Iron in Iron Ores

Dissolve 0.5 gram of the dried ore in strong hydrochloric acid, evaporate to dryness, moisten with strong hydrochloric acid, add water, and boil. Filter, wash with hot, dilute hydrochloric acid and hot water.

Save the filtrate; put the filter and contents into a platinum crucible, burn, and cool. Add hydrofluoric acid, evaporate, dissolve the residue in hydrochloric acid, boil, and filter, adding the filtrate to the first portion. Add 10 cc. strong sulphuric acid to the combined filtrates and evaporate until fumes are given off; cool and add 200 cc. water. Reduce with a Jones reductor and titrate the iron with standard permanganate solution.

Determination of Phosphorus in Ores

Take the filtrates from the silica determination, each separately, and add strong nitric acid. Evaporate till all hydrochloric acid

is expelled and the bulk of the solution is small; cool, partly neutralize with dilute ammonia, evaporate again to a small bulk, add 60 cc. ammonium molybdate solution, stir five minutes on a Ford stirring machine, and allow to settle fifteen minutes.

Filter, wash five times with 1 per cent. nitric acid, and five times with 1 per cent. potassium nitrate solution, dissolve in standard sodium hydroxide solution, and titrate back the excess with standard nitric acid solution.

Determination of Manganese in Ores

Dissolve 1 gram of dried ore in strong hydrochloric acid, evaporate to dryness, moisten with strong hydrochloric acid, add water, boil, filter, and wash with hot, dilute hydrochloric acid and hot water. Put the filter into a platinum crucible, burn, cool add hydrofluoric acid, and evaporate to remove silica. Dissolve the residue in hydrochloric acid, filter, and add the filtrate to the original solution. Add strong nitric acid to this solution contained in an Erlenmeyer flask and evaporate with further addition of strong nitric acid until all hydrochloric acid is expelled. Oxidize the manganese with potassium chlorate, boil five minutes, filter through an asbestos filter, and wash with hot water.

Put the contents of the filter (asbestos and all) back into the Erlenmeyer flask, dissolve in standard ferrous sulphate solution, and titrate back the excess with standard permanganate.

Determination of Silicon in Pig Iron

Weigh 1 gram of the drillings into a platinum evaporating dish, add 40 cc. strong hydrochloric acid, and evaporate to dryness; bake slightly, add 20 cc. strong hydrochloric acid, and boil until all the iron is in solution. Dilute with water and filter with suction; wash well with hot water; put the paper and contents into a weighed platinum crucible and burn off the carbon with the blast-lamp. Weigh the silica and calculate as Si.

Determination of Sulphur in Pig Iron

Weigh 5 grams of the drillings into a side-neck 500 cc. flask provided with a rubber stopper carrying a stop-cock funnel. Place the flask on an iron stand with the side-neck inserted into a 2 ounce measuring cylinder full of caustic soda solution of sp. gr. 1.10.

Add 80 cc. dilute hydrochloric acid (1:1) and when the action diminishes apply heat. Boil till the metal is completely dissolved and no more gas escapes into the soda solution. Disconnect the apparatus, rinse off the side neck with a wash-bottle stream, transfer the soda to a 500 cc. beaker, and wash out the cylinder twice with water. Add a few drops of starch solution as an indicator, 30 cc. strong hydrochloric acid, and titrate *rapidly* with standard iodine solution. A blank must always be made on new soda solutions.

Determination of Phosphorus in Pig Iron

Weigh 2 grams of drillings into a No. 4 beaker and add 60 cc. nitric acid (sp. gr. 1.1) boil until dissolved; filter off the graphite and heat the filtrate to boiling. Add enough dilute potassium permanganate solution to oxidize the carbon, enough having been added when the brown color of manganese dioxide is apparent. Boil a few minutes, add a few grains of sugar, and boil until the solution is clear. Add 60 cc. ammonium molybdate solution, a few drops of dilute ammonia, and stir five minutes with a Ford stirring machine. Fill, wash five times with 1 per cent. nitric acid, and five times with 1 per cent. potassium nitrate, or until the paper is free from acid. Transfer the filter and precipitate to a glass tumbler and dissolve in standard soda solution. Dilute with water and titrate back with standard nitric acid, using phenolphthalein as an indicator.

Determination of Phosphorus in Steel

The process is the same as in the case of pig iron, except that there is no graphitic carbon to be filtered off.

Determination of Manganese in Pig Iron

Weigh 1 gram of the drillings into a 150 cc. beaker, dissolve in hydrochloric acid, evaporate, and bake. Take up the residue with strong hydrochloric acid and boil until dissolved. Then dilute with water and filter into a 250 cc. Erlenmeyer flask, add strong nitric acid, and boil till all hydrochloric acid is driven off, repeating the addition of strong nitric acid as may be necessary.

Oxidize the manganese with potassium chlorate. Boil eight minutes and filter through an asbestos filter. Wash well, transfer the filter and precipitate to the flask, dissolve in standard

ferrous sulphate, dilute slightly, and titrate back the excess with standard permanganate.

Determination of Manganese in Steel

Dissolve 2 grams of drillings in 60 cc. nitric acid (sp. gr. 1.20), add 60 cc. strong nitric acid, boil, and oxidize with potassium chlorate, proceeding further in the same manner as in the case of pig metal.

Determination of Silicon in Steel

Weigh 4.702 grams of the drillings into a No. 4 Griffin beaker, dissolve in hydrochloric acid, evaporate to dryness, and bake. Cool, moisten with strong hydrochloric acid, and bake again. Take up with strong hydrochloric acid, boil, dilute, and filter by suction, washing well with hot, dilute hydrochloric acid and hot water. Burn, weigh, volatilize silica with hydrofluoric acid, and weigh again. The difference in weight is the percentage of silicon.

Determination of Nickel in Steel

Dissolve 5 grams of the drillings in 50 cc. hydrochloric acid. Oxidize with nitric acid (sp. gr. 1.42), evaporate to dryness, dissolve in strong hydrochloric acid, dilute, and filter off silica. The filtrate is evaporated to a sirup and brought into a separatory funnel; wash out the beaker with hydrochloric acid; the solution in the funnel should amount to not more than 55 or 60 cc. and should contain from 22 to 25 cc. hydrochloric acid. Now add 100 cc. ether, put in the stopper and shake; allow to stand for a few minutes, draw off the acid solution, throw away the ether, and repeat the extraction with ether, and to the second extraction it is well to add a few drops of hydrochloric acid, to make up for that removed by the ether. After the second extraction the iron is almost totally removed. Draw off the acid solution into a beaker, boil (to drive off ether), dilute, and make strongly ammoniacal to precipitate any iron present. If this precipitate is too large it is well to dissolve it in dilute hydrochloric acid on the filter and reprecipitate, using ammonia in large excess. Render the filtrate acid with hydrochloric acid, precipitate the copper with hydrogen sulphide, filter, wash, nearly neutralize the filtrate with ammonia, add 0.5 gram sodium acetate, and precipitate the nickel with hydrogen sulphide at nearly boiling-point. Fil-

ter, wash with hydrogen sulphide water (made slightly acid with acetic acid), dry, burn, and weigh as NiO.

Determination of Tungsten in Steel

Dissolve 5 grams of the drillings in a mixture of 30 cc. hydrochloric acid and 60 cc. nitric acid in a porcelain dish, and evaporate to dryness. Take up with strong hydrochloric acid, add water, boil, and filter, washing with dilute hydrochloric acid. Extract the precipitate on the filter with ammonia and run into a weighed platinum dish. Evaporate, ignite, and weigh as WO_3.

Determination of Chromium in Steel

Dissolve 5 grams of the drillings in dilute hydrochloric acid in an Erlenmeyer flask fitted with an arrangement to introduce a carbon dioxide stream during the solution in order to prevent oxidation of the iron; nearly neutralize with sodium carbonate and render alkaline with powdered barium carbonate. Dilute to the capacity of the flask, shake well, and allow to stand over night, shaking occasionally. Filter and wash well with hot water, dry, ignite, and fuse with sodium carbonate and potassium nitrate. Extract with hot water, boil, and filter off the iron oxide. Make the filtrate acid with hydrochloric acid and evaporate to dryness; take up with dilute hydrochloric acid and filter. Heat the filtrate to boiling, reduce with sulphurous acid until the yellow color disappears, and add ammonia in slight excess. Boil, filter, wash with hot water, and weigh as Cr_2O_3.

Determination of Carbon by Combustion

The process followed is that described by Dr. C. B. Dudley, Altoona, Pa.

XIV. Methods Used at the Laboratory of the Firth Sterling Steel Works, Demmler, Pa.

By A. G. McKenna

Determination of Silica in Iron and Manganese Ores

To 3 grams of finely ground ore in a 250 cc. beaker, add 50 cc. of hydrochloric acid (sp. gr. 1.20), cover with a watch-glass and boil gently on a hot plate for fifteen minutes. Dilute with hot water, filter, ignite the insoluble residue, fuse with about ten times its weight of a mixture of Na_2CO_3 and K_2CO_3 in equal parts. Leach out with hot water and add to the soluble portion. Evaporate to dryness in a 15 cm. porcelain evaporating dish. Dissolve in 20 cc. strong hydrochloric acid, add 60 cc. hot water, filter, wash alternately with hot water and dilute hydrochloric acid (1:10), ignite, and weigh as SiO_2. Add a few drops of hydrofluoric acid and heat to bright redness. The loss is silica.

Determination of Iron in Iron and Manganese Ores

To 0.5 gram of ore in a small narrow covered beaker add 15 cc. hydrochloric acid (sp. gr. 1.20) and a sufficient amount of a concentrated stannous chloride solution to nearly reduce all the iron to the ferrous condition. Boil gently for half an hour, then add stannous chloride, drop by drop, till the solution is colorless, transfer to a 500 cc. beaker, and dilute to 400 cc. with cold water. Add (all at once) 15 cc. of a saturated solution of mercuric chloride. This should cause a slight white precipitate of mercurous chloride. Titrate with standardized potassium bichromate solution, of which 1 cc. equals 1 per cent. iron on 0.5 gram of sample, using very dilute potassium ferricyanide solution as an indicator, on a plate which has been greased with paraffin to cause the drops to stand upright.

Determination of Phosphorus in Iron and Manganese Ores

The method of C. B. Murray, described on page 2, is used.

Determination of Manganese in Ores

The method of C. B. Murray, described on page 3, is used.

Determination of Silicon in Pig Iron and Steel

Dissolve 1 gram of pig iron or 5 grams of steel in a 15 cm. porcelain dish in 20 or 70 cc. strong hydrochloric acid, evaporate to dryness, dissolve in 10 cc. strong hydrochloric acid, add 50 cc. hot water, filter, wash alternately with hot water and dilute hydrochloric acid, ignite and weigh. Treat with hydrofluoric acid. The loss is silica which is calculated to silicon.

Determination of Phosphorus in Pig Iron and Steel

The method described by J. M. Camp, on page 42, is used.

The molybdic acid solution is made by mixing 100 grams molybdenum trioxide to a paste with 265 cc. water, then adding 155 cc. ammonium hydroxide (sp. gr. 0.90), and stirring until all is dissolved. To this solution add 66 cc. nitric acid (sp. gr. 1.42); stir and set aside for an hour. In another vessel make a mixture of 395 cc. nitric acid (sp. gr. 1.42) and 1100 cc. water. Then pour the first solution into the second in a small stream, stirring constantly. Allow to stand for twenty-four hours, when it is ready for use.

For the precipitation of the phosphoric acid from 5 grams of iron or steel 100 cc. of the above solution are used.

Determination of Sulphur in Pig Iron and Steel

The evolution method described by J. M. Camp, on page 41, is used. If the sulphur in a shot sample is to be determined a shot sample of known sulphur content is used for standardization.

Determination of Manganese in Pig Iron and Steel

Dissolve 5 grams of the sample in a 400 cc. beaker in 60 cc. nitric acid (sp. gr. 1.20), and boil down to a small bulk. Add 100 cc. nitric acid (sp. gr. 1.40), bring to a boil, add cautiously 8 to 10 grams of potassium chlorate, boil a few moments, and filter through an asbestos plug (using suction). Dissolve the manganese dioxide from the plug of asbestos with dilute hydrochloric acid and a few pinches of potassium nitrite, precipitate the iron by ammonia, redissolve, and reprecipitate to free from traces of manganese. In the combined filtrates, precipitate the manganese as manganese hydroxide by bromine. Ignite and weigh as Mn_3O_4.

Determination of Carbon in Steel

To from 1 to 3 grams of the sample in a 250 cc. flask are added from 50 to 150 cc. of a 30 per cent. solution of the double chloride of copper and potassium. The flask is shaken for an hour at a temperature of about 60° by a revolving board. Then 5 cc. of strong hydrochloric acid are added and the solution filtered through ignited asbestos into a platinum funnel. Wash with dilute hydrochloric acid and hot water alternately, and dry for about an hour at 100°. The funnel with its contents is then inserted into the platinum tube and the combustion made in the usual manner, the products of the combustion being led through a ten-bulb tube in which have been placed about 75 cc. of a 2 per cent. barium hydroxide solution. The precipitated barium carbonate is collected on a filter, washed *thoroughly* with hot water, ignited, and weighed as $BaCO_3$. In extremely accurate analyses it is necessary to dissolve the barium carbonate in dilute nitric acid, filter, burn, and weigh the barium sulphate as some sulphur is carried over with the carbon dioxide.

Determination of Nickel in Steel

Treat 1 gram of steel with 25 cc. nitric acid (sp. gr. 1.20) and boil in a 100 cc. flask until solution is complete. Wash the contents of the flask into a one-half gallon flask containing 700 cc. hot water, add 100 cc. sodium acetate solution, and bring to a boil for one minute. Remove from the plate and allow to settle for three minutes; filter through a 38½ cm. pleated filter into a liter beaker and allow the precipitate to run dry. To the filtrate, which should be perfectly clear and almost colorless, add 3 drops phenolphthalein, then ammonium hydroxide until pink, place on a hot plate and pass a current of hydrogen sulphide through the solution for ten minutes; remove from the plate and add 12 cc. acetic acid (50 per cent.); stir and allow the precipitate to coagulate on a warm plate for ten minutes, filter through a 12.5 cm. filter, and wash with hydrogen sulphide water made slightly acid with acetic acid. Roast in a platinum crucible carefully, at a low red heat (usually at the front of the muffle), until the paper has just burned off. Take out the crucible and break up the precipitate to powder with a platinum rod, then place in the muffle and

ignite for fifteen minutes at a bright red heat, cool, and weigh. To the crucible add 3 cc. hydrochloric acid (sp. gr. 1.20), cover with a watch-glass, and warm gently on a plate until the precipitate has dissolved. Wash into a 150 cc. beaker with water, add ammonium hydroxide until the solution smells strongly, and filter from the silica and ferric hydroxide. Redissolve the precipitate in 3 cc. hydrochloric acid and repeat the precipitation with ammonium hydroxide, wash with hot water, ignite in the same crucible, and weigh. The difference in the weight gives the nickel oxide. A correction of 5 per cent. on the quantity of nickel present is made to provide for the nickel remaining lost in the basic acetate precipitate.

The sodium acetate solution is made by dissolving 3 kilograms of sodium acetate in 12 liters of water.

The ether method as described by Mr. J. M. Camp, on page 44, is also used.

XV. Methods Used at the Laboratory of the La Belle Steel Works, Allegheny, Pa.

By Geo. G. Glass and C. E. Manby

Determination of Silicon in Steel

Weigh off 1.867 grams of steel, place into a 12 cm. evaporating dish, and add 28 cc. nitrosulphuric acid. Cover with a watch-glass and when action has about ceased, place on a hot plate and boil steadily without interruption, which prevents splashing against the cover. A white crust of iron sulphate will separate in about twenty minutes and sulphuric acid fumes will appear. Now remove the dish from the hot plate and allow to cool to about 93° C. Add 10 cc. concentrated hydrochloric acid, allow to soak a few minutes, then add 30 cc. water, and bring to a boil and keep at boiling-point until the solution becomes clear. Rinse the sides of the dish with dilute hydrochloric acid, filter, and wash with water, then with dilute hydrochloric acid, and finally with water. Press between blotting-papers, burn, and weigh. The weight of the silica found, divided by 4 and multiplied by 100, gives the percentage of silicon.

The nitrosulphuric acid is prepared by mixing together 28 cc. concentrated nitric acid, 14 cc. concentrated sulphuric acid, and 58 cc. water.

Determination of Sulphur in Steel and Pig Iron

GRAVIMETRIC METHOD

Weigh off 3.435 grams steel or pig iron into a 12 cm. evaporating dish, and add slowly 40 cc. aqua regia (25 cc. nitric acid and 15 cc. hydrochloric acid). Cover with a watch-glass and evaporate to dryness, take up with 20 cc. concentrated hydrochloric acid and when all is dissolved add 5 grams sodium chloride and evaporate to a sirup. (The sodium chloride forms a double chloride which assists evaporation to a small bulk, with the smallest amount of free hydrochloric acid.) Now take up with 20 cc.

water, heat to boiling, and, when clear, filter and place on a hot plate. While at boiling-point, add 5 cc. barium chloride solution (10 per cent.). Stir well for a few minutes and allow to stand in a warm place over night. Filter, and wash the precipitate with dilute hydrochloric acid until free from iron; then with water until free from acid. Burn and weigh. The weight of barium sulphate multiplied by 4 gives the percentage of sulphur. It is advisable to make a blank determination of sulphur in acids and sodium chloride, using the same amount of reagents as used in the actual determination, and deducting the weight of barium sulphate found from that found in the steel.

EVOLUTION METHOD

Weigh off 5 grams steel or pig iron and place into a 0.5 liter evolution flask provided with the usual connections. The lower end of the evolution tube should reach to within 0.5 inch of the bottom of a 9 in. by 1 in. test-tube, in which 20 cc. cadmium chloride solution or the same amount of zinc chloride diluted with 40 cc. water, has been added. It is advisable to have the end of the evolution tube in the flask cut off obliquely to prevent any splashings of ferrous chloride being carried over into the cadmium chloride tube during the boiling at the finish (an error of 0.002 or 0.003 per cent. is often due to this cause). When connections are all secure, pour into the funnel tube 80 cc. hydrochloric acid (33 per cent.), and heat over a flame to start a lively evolution of gas. Then lower the flame sufficiently to keep up a steady flow of gas as long as any steel or iron remains undissolved. Finally raise the heat to boiling and as soon as steam is seen condensing in the delivery-tube disconnect. Transfer the contents of the test-tube to a No. 4 beaker, using water and a little dilute hydrochloric acid to dissolve any sulphide adhering to the glass. Add 4 or 5 drops of starch solution, make slightly acid with hydrochloric acid (33 per cent.), and run in the standard iodine solution from a burette. A little more hydrochloric acid may be required to dissolve floating cadmium sulphide. The blue color produced by the first addition of the iodine changes to a pale red. Each addition of the iodine tends to restore the blue color. As the end-point approaches, add 2 cc. more of starch solution and continue the addition of the iodine until the color is deep blue. The pro-

duction of the end-point usually requires 3 drops of iodine solution as may be shown by performing a similar experiment, using an equal volume of pure water (300 cc.), and under conditions similar to those of an actual determination. Each cubic centimeter of iodine solution used corresponds to 0.001 per cent. sulphur.

SOLUTIONS

Standard Iodine Solution.—Dissolve 25 grams of potassium iodide in 100 cc. of water and add 11.43 grams of iodine crystals. After complete solution make up to 2.5 liters. The strength of the standard iodine solution is conveniently determined by comparison with that of a solution of sodium thiosulphate (containing 9 grams of the salt in 1 liter of water). This latter solution having been compared with the old iodine solution, it is then easy to ascertain the strength of the new iodine solution or to bring it, by dilution, to the required strength.

One cc. should be equivalent to 0.0005 gram sulphur (or nearly so). Now ascertain the exact strength by standardizing with a standard steel.

Cadmium Chloride in Zinc Chloride Solution.—Weigh off 14 grams cadmium chloride or 20 grams zinc chloride, add 5 cc. concentrated hydrochloric acid, then 300 cc. water, and, when the whole is dissolved and thoroughly mixed, pour into 600 cc. concentrated ammonia; then fill up to 1 liter with water for the stock solution. Be careful not to reverse the order of mixing or the solutions will be cloudy.

Starch Solution.—Take 20 grams of Bermuda arrowroot per liter of water. Or in making smaller quantities place 6 grams arrowroot into an evaporating dish and merely moisten it with water so that any lumps can be broken with a glass rod; then add more water until it becomes of the consistency of milk. Pour this into 300 cc. of boiling water (pour at intervals and stir); as soon as it looks semitransparent allow to boil for ten minutes, then remove and allow to cool with a cover on the dish to prevent a film from forming on the surface. When luke-warm, transfer to a stoppered bottle and add 2 grams zinc chloride made acid with 2 cc. concentrated hydrochloric acid. Shake well and the solution is ready for use. This solution will keep indefinitely.

Determination of Phosphorus in Steel

GRAVIMETRIC METHOD

Weigh off 1.63 grams of steel or pig iron, dissolve in 25 cc. nitric acid (sp. gr. 1.2), in a porcelain dish, and evaporate to hard dryness (covered with a watch-glass). Raise the heat to redness over a Bunsen flame to destroy organic matters. Cool, take up with 15 cc. concentrated hydrochloric acid and evaporate to about 7 cc. Add 10 cc. concentrated nitric acid and boil to remove free hydrochloric acid. Remove from the lamp and cool (while covered); then add 15 cc. water to prevent injury to the filter, when separating the silica by filtration. To the filtrate add 15 cc. ammonia; then add 15 cc. concentrated nitric acid and heat to 85° C. Lastly add 50 cc. molybdate solution, shake at intervals during five minutes, and allow to settle. Filter off the yellow precipitate into a tared filter and wash with 2 per cent. nitric acid solution. Test the washings with potassium thiocyanate. Remove the filter and press between blotters; then dry for one hour in an oven at 100° C. Weigh as usual between two watch-glasses. The weight equals the percentage of phosphorus.

For a determination of phosphorus in basic steel, double the quantity of metal is used, the acid required being proportionally greater.

VOLUMETRIC METHOD

Weigh off 2.6 grams steel into a 500 cc. Erlenmeyer flask, and dissolve in a mixture of 12 cc. nitric acid and 30 cc. water. When the violent action subsides place on a hot plate, bring to boiling, add 10 cc. concentrated potassium permanganate solution, and boil until the color changes to brown; add 2 cc. hydrochloric acid and boil for one minute; then add 30 cc. water and maintain at the boiling-point; lastly, 10 cc. sodium nitrite solution. The sodium nitrite, besides causing reduction and solution of the manganese oxide in the acid fluid, promotes the subsequent precipitation of the ammonium phosphomolybdate in crystalline form and its use, suggested by C. E. Manby, has proved to be an important improvement in the process.

The solution then instantly clears up. Cool and add 20 cc. ammonia, shake until mobile, and then add 18 to 20 cc. concentrated nitric acid. Then shake until clear, place again on a hot plate

(if not quite clear), and add a few drops more of sodium nitrite solution. Heat to boiling, remove from the plate, and take the temperature, which should reach 90° C. Add 65 cc. molybdate solution, shake and allow to settle. When clear, filter and wash by decantation or suction; wash the filter four times with 2 per cent. nitric acid, then complete the washing with sodium nitrate solution (6 grams per liter), wash until free from iron and acid (using potassium thiocyanate as an indicator), or wash with a stock solution made from water and a few drops of phenolphthalein and 1 or 2 drops of the standard alkali sufficient to produce a strong pink color. A convenient vessel in which to test the drops during the washing is a small white porcelain crucible. First put in a few drops of the reagent and allow several drops from the funnel stem to fall into it. As a rule the last traces of iron and acid disappear together.

Titration.—Place the filter containing the yellow precipitate into a 250 cc. Erlenmeyer flask provided with a rubber stopper. Have two burettes, side by side, filled with standard alkali and standard nitric acid, these being of equal strength. Start by running in 10 cc. alkali solution then dilute with 30 cc. water, and shake the contents; the filter will immediately break up. Now add 2 or 3 drops of concentrated solution of phenolphthalein, titrate back with standard nitric acid until colorless again, then with alkali to produce a permanent pink (when shaken up), and cork tightly to prevent impure air bleaching out the pink. The difference of the burette readings gives the percentage of phosphorus when divided by 100.

SOLUTIONS

Molybdate Solution.—Place 100 grams of molybdic acid into a beaker, add 200 cc. water, and stir into a cream. Pour this mixture into a flask containing 100 cc. concentrated ammonia water. When all is dissolved, pour into 1.5 liters of warm dilute nitric acid (sp. gr. 1.20). Keep at 50° C. Allow the solution to stand until the following day and decant for use.

Standard Sodium Hydroxide Solution and Standard Nitric Acid.—Dissolve 20 grams caustic soda in sticks in water and dilute to 2.4 liters.

Dilute 28 cc. nitric acid (sp. gr. 1.42) to 2346 cc. Compare and make these two solutions equal in strength.

Phenolphthalein Solution.—Make a concentrated stock solution in pure alcohol, and neutralize with standard alkali until one drop gives a permanent pink color.

Determination of Phosphorus in Pig Iron

Weigh 2.6 grams of the metal, place into a 500 cc. Erlenmeyer flask, and dissolve in a mixture of 50 cc. water and 12 cc. nitric acid. When the action subsides place on a hot plate and heat to boiling. Add 10 cc. of a concentrated solution of potassium permanganate, heat for five minutes, add 2 cc. hydrochloric acid and continue the boiling; then add 40 cc. water, boil, and add 10 cc. sodium nitrite. When clear, cool and filter. The clear filtrate is proceeded with at this stage in the same manner as described for steels.

Determination of Phosphorus in Ores

A fusion is made with 2.6 grams of ore, or half that weight as occasion requires. Dissolve in hydrochloric acid, evaporate to dryness, and filter off the silica if considerable; if low in silica evaporate nearly to dryness; then add 20 cc. nitric acid and boil until brown fumes cease to appear. Add 2 cc. permanganate solution, boil a few minutes, then add 30 cc. water and 5 or 6 drops hydrochloric acid; continue the boiling, add 10 cc. sodium nitrite solution, and proceed in the same manner as in the case of steel.

Determination of Carbon in Steel

COMBUSTION METHOD

Weigh off 2 grams steel drillings, place into a No. 2 beaker, and pour in 100 cc. of a saturated solution of double chloride of copper and potassium. Allow to digest with frequent stirring until the iron is dissolved, then add 10 cc. concentrated hydrochloric acid, stir frequently, and, when dissolved, filter through a platinum boat (using suction). Wash first with dilute hydrochloric acid, then with water till free from acid. Remove the boat from the holder and dry in an oven at 100° C. for about one hour. When dry, place the boat into a combustion tube and burn in a stream of oxygen in the usual way, passing the carbon dioxide into a 10-bulb tube containing 100 cc. of barium hy-

droxide (saturated solution). When combustion is completed, filter off the barium carbonate as rapidly as possible (using suction) and wash with hot water (which has previously been boiled to expel any carbon dioxide) until the washings (4 drops) leave no residue when evaporated on a platinum spatula. Burn in a platinum crucible over a Bunsen burner (do not use a blast-lamp), and weigh as $BaCO_3$ containing 6.09 per cent. carbon.

COLOR METHOD

Test pieces are heated to a bright red heat and suddenly quenched in cold water, then placed into an oven and annealed (at different temperatures according to the amount of carbon present, higher carbons requiring a higher annealing heat), and allowed to cool under powdered lime. Compare with standards treated in the same manner.

Determination of Manganese in Steel

COLOR METHOD

Weigh off 0.1 gram of steel, place into a 12 cm. test-tube, and add 20 cc. nitric acid (sp. gr. 1.2); heat in a sand-bath until dissolved; then add a few grains of white sand to prevent bumping during the boiling, continue boiling until all traces of brown fumes disappear. Then cautiously add lead peroxide (about 1 gram) and boil briskly for two and one-half minutes. Place the tube into cold water and allow to settle. Compare with a solution of a standard steel treated in the same manner. When settled, carefully decant into the comparison tubes; each cubic centimeter is equivalent to 0.01 per cent. manganese.

GRAVIMETRIC METHOD

Weigh 2 grams of steel and dissolve in 30 cc. nitric acid (sp. gr. 1.2) in a No. 4 beaker having a watch-glass cover. Evaporate until the fluid is sirupy and add 50 cc. concentrated nitric acid. Boil, add cautiously 2 or 3 grams of potassium chlorate while the fluid is boiling, and allow to cool. Filter through broken glass, supporting a layer of fine asbestos, and wash with nitric acid to remove iron. The manganese dioxide is then dissolved by adding a few cubic centimeters of a 2 per cent. sodium nitrite solution and a little nitric acid. Wash well with hot water and heat the filtrate to expel nitrous fumes. Cool and make a basic acetate

separation of any iron present. Heat to boiling and filter. To the clear filtrate add 1 gram of ammonium phosphate crystals and a few drops of acetic acid. Warm gently and add a few cubic centimeters of strong ammonia until decidedly alkaline. The precipitate of ammonium manganese phosphate should now separate in a crystalline state. Filter and wash with 2 per cent. ammonia water until 4 drops evaporated upon a platinum spatula leave no fixed residue. Burn in a platinum crucible, heating gently at first, and finally at a higher temperature until white. A blast-lamp should not be used, as the precipitate is liable to undergo partial fusion at a very strong heat. Weigh as $Mn_2P_2O_7$ containing 38.73 per cent. manganese.

Determination of Nickel in Steel

Weigh off 1 gram steel, place into a 12 cm. evaporating dish, dissolve in 20 cc. nitric acid (sp. gr. 1.20), keep covered with a watch-glass, and evaporate to dryness. Take up with 15 cc. concentrated hydrochloric acid, evaporate (while covered) to 5 cc., and allow to cool. Now add 30 cc. hydrochloric acid (sp. gr. 1.10) and decant into a separatory funnel of 100 cc. capacity. Rinse out the dish with hydrochloric acid (sp. gr. 1.10) using as little as possible (5 to 10 cc.). Measure off 40-45 cc. ether and wash any remaining chlorides into the funnel; this will make 80-85 cc. of solution. Place the stopper into the funnel and cool it under the tap; then shake well and allow to stand a few minutes. When the dividing line between the two liquids is quite distinct, run off the lower liquid, which contains all the nickel chloride and free hydrochloric acid, until 1 drop of iron solution runs through the stop-cock. Wash off the tube with water and add 20 cc. water to the solution to further dilute the hydrochloric acid; then add ammonia cautiously to separate iron and silica. Filter and wash with water; then make acid with acetic acid until the blue color changes to pale green. Boil off the ether and add about 20 drops of thiacetic acid and boil gently until the black nickel sulphide separates. Allow to stand a short time, filter, and wash with hydrogen sulphide water (made acid with a little acetic acid), until free from ammonium chloride. Burn and weigh as NiO, containing 78.6 per cent. nickel.

Volumetric Determination of Tungsten

Tungstic acid may be readily determined volumetrically by standard alkali solution. The following method gives very rapid results, requiring only two hours for the complete determination. Duplicate determinations have been found to agree within 0.1 per cent.

Weigh off 1.84 grams of steel and dissolve in 35 cc. nitric acid (sp. gr. 1.20) in an evaporating dish provided with a glass cover. Evaporate but once to *hard dryness* on a hot plate until the resulting crust of oxides becomes partly detached. Cool, and take up with 25 cc. hydrochloric acid, boil for ten minutes, or until signs of bumping appear, add 30 cc. water, and continue boiling a few minutes. Filter and wash with a hot mixture of 1 part hydrochloric acid and 2 parts water until free from iron, then with sodium nitrate solution (6 grams per liter). This will remove all free acid. Test the filtered drops occasionally with phenolphthalein, then titrate in the same manner as described for phosphorus (the reading on burettes in cubic centimeters gives the percentage of tungsten). Tungsten steels contain usually 5 per cent. tungsten.

XVI. Methods Used at the Laboratory of the Park Steel Company, Pittsburg, Pa.

By Charles M. Johnson

Determination of Silica in Iron Ores

One to three grams of the finely pulverized ore are digested upon the water-bath in a covered beaker with 10-30 cc. of concentrated hydrochloric acid until decomposition is complete. The solution and silicious residue are then transferred to a porcelain dish, and the solution evaporated on the graphite-bath (substitute for the sand-bath) to dryness. The residue is taken up with concentrated hydrochloric acid and water, the solution evaporated as before, and, after redissolving the dry mass in concentrated acid and dilution with several volumes of water, the silicious residue is collected upon a Swedish filter, thoroughly washed, and ignited in a platinum crucible. After ignition the residue is subjected to a fusion with ten to fifteen times its weight of sodium carbonate. The fusion is dissolved in water and hydrochloric acid, the solution evaporated to dryness on the water-bath, and the separation of the silica further conducted as usual under the given circumstances. The insoluble residue remaining after the fusion, etc., is weighed ordinarily as SiO_2.

In still more accurate determinations, the silica thus obtained is treated with hydrofluoric and sulphuric acids. The loss after evaporation and ignition is silica.

Determination of Iron in Ores

Fuse 0.4 to 0.5 gram of the sample, in case of high-grade ores, with 10 to 15 grams of sodium carbonate. After the fusion is complete dissolve in the least possible quantity of water in a porcelain dish. Add 30 cc. concentrated sulphuric acid diluted with an equal bulk of water and 3 cc. hydrochloric acid, and evaporate until sulphuric acid fumes appear. Cool and dilute to

100 cc. Add 20 grams of fine shot zinc to cause reduction of the ferric salt. To hasten the solution of the zinc, heat to boiling. During the boiling a stream of carbon dioxide is passed into the flask by a glass-tube inserted through a perforated watch-glass, which rests upon the neck of the flask. The glass tube reaches nearly to the surface of, but does not dip into, the solution. The iron is determined volumetrically by a standard solution of potassium permanganate, of which 1 cc. corresponds to 0.0068 gram iron. For standardizing this solution, oxalic acid is used.

The method is applicable to the determination of iron in clay, in graphite crucible material and in various minerals. Where the proportion of iron to be determined is small, a weaker solution of permanganate is used. A blank determination is always made in the case of the zinc and sulphuric acid used.

Determination of Phosphorus in Ores

This element is separated as ammonium phosphomolybdate and weighed in the same form.

1.63 grams of ore are weighed off into a small porcelain dish and treated with about 20 cc. of concentrated hydrochloric acid, and the mixture, with frequent stirring, is heated on the water-bath until all but silicious matter has dissolved. Add 0.5 gram of potassium chlorate and heat until action has ceased. The solution is evaporated to dryness, and the residue redissolved in 20-30 cc. of hydrochloric acid. This second hydrochloric acid solution is evaporated until the separation of basic chloride of iron begins. With 2 or 3 drops of acid, the solution is restored, 30-40 cc. of water are added, and the insoluble silicious residue is filtered off. The filtrate, which should have a volume of about 60 cc., is ready for the precipitation which is effected as described below for steel.

Determination of Manganese in Ores

When the manganese amounts to more than 3 per cent. of the ore, Volhard's method is used. Fuse the ore with sodium carbonate, soften the fusion in water and treat with sulphuric and hydrochloric acids exactly as in the case of the determination of iron in ores, adding a little potassium chlorate to insure complete oxidation of the iron before evaporating the solution to the point where sulphuric acid fumes are produced. Transfer to a liter

flask and fill two-thirds full. Add an excess of zinc oxide free from manganese. Mix thoroughly and dilute to 1 liter. Make a correction for the volume occupied by the precipitate (0.6 cc. for 1 gram of iron). Pour through a dry filter and receive three portions of 200 cc. each in beakers, one portion being intended for a preliminary trial and the other two for duplicate determinations. Add 1 or 2 drops of nitric acid and titrate with permanganate at a temperature just below the boiling-point.

COLORIMETRIC METHOD

From 0.05 to 0.10 gram of ore is placed into a 15 cm. by 125 cm. test-tube and dissolved in 2 to 3 cc. concentrated hydrochloric acid, which is then expelled by boiling with an excess of concentrated nitric acid (sp. gr. 1.42). The nitric acid solution is poured into a 25 cm. by 2.5 cm. test-tube, rinsed out from the smaller tube with 32 per cent. nitric acid, and diluted with the same to a volume of about 35 cc. By the addition of lead peroxide and boiling, manganese is oxidized to permanganic acid and determined in this form, as directed for the estimation of manganese in steel.

Determination of Silicon in Pig Iron

One gram of metal is dissolved in a small covered porcelain dish in 10 cc. of dilute sulphuric acid (1:3) with the addition of an equal volume of water. The action of the acid is hastened by heating. When the evolution of hydrogen has ceased, the cover glass is rinsed off into the dish, and the latter placed on the graphite-bath, where the contents of the dish are heated until dense white fumes of sulphuric acid form abundantly. The dish is removed from the bath, allowed to cool somewhat, and the residue treated with water. Heat and stirring are applied until all iron sulphate has dissolved; the insoluble residue is filtered off, washed with water and dilute hydrochloric acid until free from iron, ignited and weighed as silica. The silica so obtained is usually found to be contaminated by a small and almost constant proportion of the oxides of iron and aluminum. For this reason a deduction of 0.05 per cent. is made from the percentage of the silicon calculated from the silica found.

This correction represents the average result of determinations of the impurity contained in the silica derived from pig iron.

Determination of Sulphur in Pig Iron

The method adopted for the estimation varies with the variety of iron and the accuracy required. For gray iron and "commercial" accuracy, the evolution-volumetric method is applied; for white iron and also gray varieties of pig iron, when the utmost accuracy is demanded, the aqua regia method is made use of.

EVOLUTION-VOLUMETRIC METHOD

The details of the process are given below in the description of methods for the analysis of steel, *q. v.*

AQUA REGIA METHOD

The sample (about 5 grams) is dissolved in 100 cc. concentrated nitric acid (sp. gr. 1.42) with the addition of 2 or 3 cc. hydrochloric acid, and by the aid of heat, when necessary, to start the dissolving of the borings. When the action of the acid has ended, about 2 grams of sodium carbonate are added, and the solution is warmed until the escape of carbon dioxide has ceased. Silica is separated as usual by evaporation to dryness, solution of the residue in hydrochloric acid, and filtration. The slightly acid filtrate is diluted to 75-100 cc. for each gram of metal taken for the determination, and treated, while at a boiling temperature, with a hot solution of barium chloride in moderate excess. After the mixture has stood several hours, the precipitate of barium sulphate is collected on a Swedish washed filter and washed with cold water and with 1 per cent. hydrochloric acid, using this diluted acid once for every ten washings with water. Should the precipitate contain iron, a separation of the latter by fusion with 0.3 gram sodium carbonate, etc., is undertaken after ignition.

Determination of Manganese in Pig Iron

The same considerations and practice apply in the determination of manganese in pig iron as in the estimation of that element in steel. See p. 109.

Determination of Carbon in Steel

According to the proportion of carbon present, 1 to 10 grams of steel are treated with a solution of cupric potassium chloride (30 to 40 cc. for each gram of metal).

The mixture of chloride and steel borings, maintained at room

temperature, is constantly stirred by a stirring machine until the metallic copper, which separates in the reaction, is redissolved.

The filtration is effected by means of a glass carbon filter tube, of which the upper and wider portion is 18 mm. in diameter. A porcelain disk, having numerous perforations three-quarters mm. wide, is placed at the bottom of the filter. A small filter plate answers the purpose. The asbestos wool to be used for the filtration is heated to redness and then cut into short pieces with the scissors (a manipulation rendered much easier by the preliminary heating). After a second ignition it is agitated with water. Poured as a pulp over the perforated plate, a suitable felt is formed ready for the filtration.

The carbonaceous residue from the steel is washed thoroughly with dilute hydrochloric acid. In the case of chrome or tungsten steels the treatment with copper chloride leads to the production of a residue containing a compound of these metals with iron and carbon. Washing of the residue with hydrochloric acid may in such case cause an evolution of a gaseous hydrocarbon and consequent loss of carbon. Water alone must then be used in washing.

The acid used for washing the carbonaceous residue of steels *not* containing chromium or tungsten is made by mixing 90 cc. of concentrated hydrochloric acid with water to make up to 400 cc. Of this stock solution 5 cc. are diluted to 25 cc. for use.

The residue, after washing, is removed, while wet, from the filter tube by taking out the filter-plate. The asbestos mat, with the carbon, is transferred to a platinum boat and dried at 100° C., and is then ready for the combustion.

The combustion is carried out in a porcelain tube of the usual dimensions, heated in a ten-burner Bunsen combustion-furnace, and supplied with a slow stream of oxygen purified by passage over red-hot copper oxide and through absorbents for water and carbon dioxide, in the following order: Through potassium hydroxide solution ($1KOH:2H_2O$), and over granulated calcium chloride and soda-lime.

The combustion-tube, projecting 4 or 5 inches beyond the furnace at either end, is filled, excepting the projecting ends and enough space in the rear for the reception of the boat, with coarsely granular copper oxide which is kept in place by short

spiral rolls of copper gauze. To prevent too great heating of the ends of the tube a strip of blotting-paper is wrapped around the tube at each end and dips into a small crucible filled with water and suspended below. The cooling effect due to evaporation of the water protects the corks against burning. Rubber stoppers at the rear and front ends of the tube connect, respectively, with the supply of oxygen and the apparatus for the purification and absorption of the carbon dioxide formed in the combustion tube. The possible impurities which require removal are hydrochloric acid and chlorine. The gases issuing from the front end of the tube are, therefore, caused to pass first through a glass tube 12.5 cm. long and 1.25 cm. in diameter, containing granulated zinc; then through a U-tube of the same size containing calcium chloride and then through a tube containing phosphoric anhydride. The Geissler potash bulbs follow, containing potassium hydroxide solution (1:2) to prevent loss of moisture from the solution by the continuous passage of gas through the apparatus; the bulbs are fitted with a cover-tube with ground joint, containing solid potassium hydroxide. Connected with the exit end of the potash bulbs, a 15 cm. straight calcium chloride tube, filled also with pieces of potassium hydroxide, protects them against the possibility of the entrance of moisture and carbon dioxide from the atmosphere. It concludes the train of apparatus.

After introducing the boat with its carbonaceous residue, weighing and attaching the potash bulbs, securing all connections and starting a slow stream of oxygen through the apparatus, the combustion is begun by heating the front end of the combustion tube to redness. The rest of the tube containing the boat is then gradually heated to the same temperature. For fifteen to twenty minutes a red heat is maintained and the passage of oxygen continued. In case of high carbon, chrome and tungsten steels, heat forty minutes. The oxygen is then cut off and air from an independent drying and purifying apparatus (a duplicate of that described for use with oxygen) is drawn, during forty-five to sixty minutes, slowly through the entire apparatus. By this manipulation all carbon dioxide is brought into the potash bulbs, and the latter are filled with air. To insure a complete displacement of the oxygen in the potash bulbs, after the main aspira-

tion, air, which has been freed from carbon dioxide, is drawn for some minutes through the drying apparatus directly behind the bulbs, and the bulbs themselves. The potash apparatus is detached and allowed to stand fifteen to twenty minutes in the balance-case where it had stood for at least the same length of time before the first weighing. The increase in weight is ascertained and therefrom the percentage of carbon is deduced.

The cupric potassium chloride solution is made by dissolving 1200 grams of the double salt in 3 liters of water, adding 350 cc. of concentrated hydrochloric acid and filtering through ignited asbestos.

Determination of Sulphur in Steel

The determination is effected by separating the element as cadmium sulphide and estimating the sulphur in the latter volumetrically with iodine solution.

The metal is dissolved in dilute hydrochloric acid; the gases evolved are passed into a strongly ammoniacal solution of cadmium chloride in which the sulphur, entering as hydrogen sulphide, is precipitated. The precipitate is filtered off, dissolved in a large volume of dilute hydrochloric acid, and the hydrogen sulphide again set free, measured as indicated above. The solution of the sample is carried out in a 250 cc. Florence flask.

Into the neck of the flask is fitted a rubber stopper with three perforations. One of the latter receives the stem of the separating funnel with wide mouth and a bulb which should have a capacity of about 50 cc.; through another perforation passes the ¼ inch conduction tube, connecting the evolution flask directly under the stopper with the absorption tube; a third ⅛ inch tube, the hydrogen tube, passes through the stopper to the bottom of the flask where it is drawn out to a point and bent upwards about ⅛ of an inch. Above the stopper it is connected with a supply of hydrogen.

The conduction tube, which is in one piece, rises perpendicularly to about one-half inch from the stopper, bends away from the perpendicular about 60°, extending in this direction 5 or 6 inches, when it dips directly downward into the absorption tube, a 10 in. by 1 in. lipped test-tube of stout glass. Between the first and second bends in the conduction tube are blown two ¾ inch bulbs.

The evolution flask and absorption tube are securely held in the required position by specially adapted racks (the flasks over Argand gas-burners) during the precipitation of the sulphur.

In carrying out a determination with the above apparatus, 3 to 5 grams of the sample are placed into the flask and about 50 cc. of cadmium chloride solution into the absorption tube. Connections being made and the hydrogen tube closed, 50 cc. of dilute hydrochloric acid (1:1) are gradually or at once, according to the probable rate of evolution of gas, run into the flask through the separating funnel, and a brisk generation of gas is maintained, if necessary, by the aid of heat. When the sample has dissolved, hydrogen is turned on in a slow stream, and the solution boiled until the bulbs of the conduction tube become hot. The flame under the flask is then turned out, and the passage of hydrogen continued moderately for ten to fifteen minutes. The precipitated cadmium sulphide is transferred to a rapid German filter. To this end, after disconnecting the absorption apparatus from the flask, the conduction tube is withdrawn from the absorption tube and laid aside, the adhering precipitate being washed down beforehand into the tube as completely as possible; the portion adhering firmly to the latter, unless it be considerable, is not removed to the filter but left to be dissolved off, together with that remaining on the conduction tube, at the final solution of the precipitate. After several washings, the filter and precipitate are placed into a 600 cc. beaker. According to the quantity of precipitate, 200 to 400 cc. of water are poured over it, 3 cc. of starch solution (1:150) added, and the mixture stirred until the filter and precipitate are well disintegrated. Fifty cc. of dilute hydrochloric acid (1:1) are poured into the absorption tube, and water is added to fill the tube to within an inch of the top. The conduction tube, which had been laid aside before the filtration, is quickly dipped into the diluted acid to dissolve any adhering cadmium sulphide. The contents of the absorption tube are added to the water and precipitate in the beaker. The precipitate dissolves mainly at once and entirely on stirring. Without waiting until all cadmium sulphide has dissolved, the estimation of the sulphur is at once begun by titration of the liberated hydrogen sulphide with iodine solution.

SOLUTIONS

The cadmium chloride solution is made by dissolving 80 grams of cadmium chloride in 1.5 liters of strong ammonia water and 2.5 liters of water.

The standard iodine solution is prepared by dissolving 1 gram of resublimed iodine in 50 cc. of an aqueous solution of potassium iodide ($1KI + 10H_2O$), and diluting to 1 liter. While pure reagents and careful manipulation insure a solution of the desired strength, the latter is nevertheless confirmed by direct experiment before the solution is used. For this purpose a standard steel, previously tested by the aqua regia method, is used.

Determination of Phosphorus in Steel

This element is determined by weighing as ammonium phosphomolybdate.

1.63 grams of steel are dissolved in a covered beaker in 45 cc. of 20 per cent. nitric acid, the action of the acid being hastened by warming. When a perfect solution has been obtained and brought to the boiling-point, an excess of a saturated solution of potassium permanganate is added and the boiling continued two or three minutes. While still boiling, the mixture is treated with sufficient ferrous sulphate in saturated, slightly acidified solution (5 cc. sulphuric acid per liter) to dissolve the precipitated manganese dioxide resulting from the action of potassium permanganate on the original nitric acid solution of the metal. The dioxide disappears, leaving usually a clear solution. If it is not clear the solution is filtered for the removal of "scale," etc., sometimes unavoidably weighed off with the steel. A clear solution having been obtained, about 15 cc. of water are added and the contents of the beaker again heated to boiling. The beaker is removed from the source of heat and rinsed down with water. The volume of the solution should be about 60 cc. After stirring for a few seconds the temperature for precipitation (under 80° C.) will exist in the solution. 45 to 50 cc. of molybdate solution are then added and the mixture thoroughly and repeatedly stirred. The supernatant liquid is poured (with as little disturbance of the precipitate as possible), when it has become clear, through a washed Swedish filter. The latter is washed twenty-five times with a 1 per cent. (by volume) nitric acid, when the precipitate is

transferred to the filter, and the washing continued until the filter and precipitate are free from iron. The filter with its contents is dried for one hour at 100° C., and weighed between accurately ground watch-glasses, the drying and weighing of the filter alone having been conducted under similar conditions. The number expressing the weight of the precipitate in grams also represents the percentage of phosphorus.

MOLYBDATE SOLUTION

Dissolve 120 grams of ignited molybdic acid and 60 grams of the unignited acid in 900 cc. of ammonia water (sp. gr. 0.96). Add this solution to 2700 cc. of 32 per cent. nitric acid and dilute the whole to 4 liters. This solution precipitates the phosphoric acid with very little stirring. When *ignited* molybdic acid alone is used in making up the reagent, the ammonium phosphomolybdate is precipitated as an extremely fine powder. The *unignited* acid yields a precipitate of coarser grain but more liable to dissolve in the acid-washing fluid unless the stirring is prolonged. The above mixture of ignited and unignited molybdic acid is found to yield very satisfactory results.

Determination of Manganese in Steel

In the determination of manganese the colorimetric method is used almost exclusively, the quantities encountered seldom exceeding 3 per cent. For higher percentages, as in the case of ores also, a gravimetric method is used.

COLORIMETRIC METHOD[1]

The process consists in converting the manganese present into permanganic acid and deriving colorimetrically, by means of a solution of potassium permanganate containing a known quantity of manganese, the amount of manganese in the permanganic acid obtained from a given weight of steel.

One-tenth gram of metal is dissolved in a 10 in. by 1 in. test-tube in 35-40 cc. of 32 per cent. nitric acid, and the solution heated to boiling over a small flame from a Bunsen burner. When the formation of nitrous fumes ceases, the heat is removed, and 0.2-0.5 gram of lead peroxide is added. Heat is again applied, and the mixture boiled for three or four minutes. The tube is

[1] The use of potassium permanganate in this connection was, I believe, first suggested by Mr. B. B. Wright, formerly chemist to the Black Diamond Steel Works.

then stood aside, closely covered and in the dark, in cold water until the excess of lead peroxide has settled down. When clear, the acid solution above the lead peroxide (now containing the manganese as permanganic acid) is decanted into a 50 cc. comparing tube, which is graduated to 0.5 cc., and is one of a set of three exactly similar tubes; the remaining two receive the solutions of potassium permanganate to be used in determining the quantity of manganese, in the form of permanganic acid, obtained by the process just described.

The permanganate solutions are prepared from a stock solution of such strength that 10 cc. of the same, when diluted to 250 cc., will produce a solution of which 1 cc. contains 0.00001 gram of manganese as permanganic acid. In practice this dilute solution is called the *normal* standard. From the normal, others are prepared (by dilution with water in the comparing tubes) having a simple ratio, 1:2, 1:3, 1:4, etc., to normal. All of these solutions are adjusted directly before use from the stock solution. The latter is made 1 liter at a time, and may, with proper precautions, be kept for several weeks without appreciable change. Equipped with this solution and its derivatives, the procedure in estimating the quantity of manganese in the permanganic solution, yielded by a sample of steel under the conditions above detailed, is obvious and simple. In one of the comparing tubes are placed 30 to 40 cc. of a standard permanganate solution of lighter tint than the permanganic solution. The latter is then diluted with water until the tints in both tubes cannot be distinguished from each other, the examination or "comparing" of the shades of color being carried out over a sheet of white paper on the diffuse light of a window. The ratio of the volumes of the two solutions is plainly equal to the ratio of the quantities of manganese contained in them. The volumes being read off from the graduated comparing tubes, and the quantity of manganese in one solution being known, the quantity in the other is readily calculated. If the normal permanganate be used, the number expressing the volume of the solution (in cubic centimeters) containing the unknown quantity of manganese divided by 100 is the required percentage when 0.1 gram of steel is taken for the determination; if a standard of lighter tint be used, the volume must first be multiplied by the fraction showing its relation to the normal.

For example 35 cc. with the normal standard represent 0.35 per cent. manganese and with a 3:4 standard, 0.26 per cent. In the case of the higher percentages of manganese, which may still be determined colorimetrically with convenience and accuracy, some modifications of the general method already given are advisable or necessary. It is advisable to weigh off for the determination at least 1 gram of borings that a representative result may be obtained from the sample. A solution in 32 per cent. nitric acid is prepared and diluted in a 500 cc. flask to the mark. Aliquot parts equivalent to from 0.05 to 0.1 gram are then taken for single determinations. After evaporation to from 5 to 10 cc., transfer to a test-tube, and dilute to about 80 cc. with 32 per cent. nitric acid, when the solution will be ready for oxidation. Experiments thus far have shown that under the above conditions ten to twenty minutes' boiling with 0.5 gram of peroxide suffices to oxidize at least 2.5 per cent. manganese in 0.1 gram. The test of complete oxidation is made the obtaining, within the limits of error, of the same result, whether 0.1 gram or half that quantity be used for the determination, the conditions being in each case in all other respects the same.

Further, after the decantation of the permanganic solution, a slightly varying quantity of the latter is left adhering to the tube and the residue of peroxide. When higher percentages are concerned, the quantity of manganese represented by the fluid residue is not inconsiderable, and cannot be neglected in accurate determinations, as in the case of the lower percentages. The tube and residual peroxide should therefore be rinsed with a few cubic centimeters of water or 32 per cent. nitric acid. The rinsings are filtered through carefully washed asbestos into the decanted solution. The asbestos for the filtration is prepared by boiling with strong hydrochloric acid, washing with water, and ignition. If chromium is present to the amount of 0.5 per cent. it interferes with the colorimetric estimation of the manganese as above described. With 1 per cent. of chromium the method would be inapplicable. It is therefore necessary in such cases to remove the chromium before proceeding to the manganese determination. One gram of the steel is dissolved in nitric acid (sp. gr. 1.2) and the solution transferred to a liter flask. Dilute to fill the flask two-thirds full. Add an excess of zinc oxide free from man-

ganese (not the ignited oxide). Then dilute to 1 liter, and make a correction for the volume occupied by the precipitate (0.6 cc. for each gram of iron). Filter through a dry filter and receive aliquot portions (200 cc. each). Evaporate in a porcelain dish, covered with a paper cone to exclude dust, to about 20 cc. Transfer to a test-tube, 25 cm. long by 2.5 cm. wide, and fill up to 35 cc. with nitric acid (sp. gr. 1.20). The manganese is now to be converted into permanganic acid by boiling with lead dioxide and nitric acid as already described and the color comparison made as before.

Determination of Copper in Steel

Fifteen grams of steel drillings are treated in a beaker with 125 cc. of dilute sulphuric acid (1:3 by volume), and as the action diminishes the beaker is warmed to promote solution. Evaporate in a No. 7 porcelain dish over a graphite-bath until strong fumes of sulphuric acid appear. Cool, take up with water, and filter. The residue may contain copper if, after burning, it is not white. In that case fuse, dissolve, and separate silica by the usual method, and add the filtrate to the main solution. The silica is to be washed until free from iron. Nearly neutralize the solution with ammonia, heat, and add sodium thiosulphate, which will precipitate the copper as sulphide. Heat until the precipitate subsides, filter, and wash with cold water containing a little sulphurous acid. Ignite the copper sulphide in a porcelain crucible. Dissolve in 1 cc. concentrated hydrochloric acid, dilute, and add a slight excess of ammonia water. Filter (using a 5 cm. filter), wash with a mixture of 1 part solution of ammonia and 25 parts water, and obtain a filtrate of about 10 cc. Transfer to a comparison tube graduated to 0.2 cc. (such as is used for manganese determinations) and compare the color with that of a standard ammonia copper solution, of which 1 cc. contains 0.0001 gram of copper. The portion of standard solution used must contain approximately the same amount of ammonia per cubic centimeter as the ammonia solution of the copper obtained from the sample, since otherwise a comparison of the colors will lead to an incorrect result. The process, as described, is used in the case of steel containing not more than 0.06 per cent. of copper. For a standard to be used in making the comparison, take 10 cc. of stock

copper solution (1 cc. of which contains 0.001 gram of copper), and dilute to 100 cc. with a mixture of 1 volume of ammonia water and 25 volumes of water. One cc. of this solution contains 0.0001 gram of copper. The details of the process of comparison and of the calculations are similar to those of a carbon determination by color. The solution of the test sample is to be diluted with the ammonia wash-water (1:25) until its color matches that of the solution of the standard. The proportion of the copper is then ascertained by a very simple calculation.

XVII. Methods Used at the Laboratory of the Vandergrift-Apollo Steel Works of the American Sheet Steel Company, Vandergrift, Pa.

By W. H. Ginder

Determination of Silica in Ores

Dissolve 1 gram of the finely pulverized sample in 30 cc. concentrated hydrochloric acid, evaporate to dryness, and add 25 cc. concentrated hydrochloric acid. Boil, dilute, filter, and wash with hot dilute hydrochloric acid and water. Burn and fuse the residue, dissolve the fusion in water and a little hydrochloric acid and evaporate to dryness. Redissolve in hydrochloric acid and water, filter, wash well with cold water, burn, and weigh. Treat the residue with hydrofluoric acid and a few drops of sulphuric acid. The loss in weight represents the amount of silica.

Determination of Iron in Ores

Reduce the iron in the combined filtrates from the silica, with granulated zinc, and add potassium dichromate solution until a drop of the iron solution added to a drop of potassium ferricyanide solution fails to produce a blue color in thirty seconds. The number of cubic centimeters of potassium dichromate used represents the percentage of iron.

Potassium Dichromate Solution.—Dissolve 17.588 grams of the fused salt in 2 liters of water and standardize with metallic iron.

Determination of Phosphorus in Iron Ores

Dissolve 1.63 grams of the sample in 40 cc. concentrated hydrochloric acid in a 250 cc. beaker by gently boiling for half an hour, dilute with water, and filter into a 250 cc. beaker. Wash with hot water and evaporate to dryness over a flame. Ignite the residue and fuse with 10 grams sodium carbonate, dissolve the fusion in a 200 cc. beaker, and evaporate to dryness. Add 25 cc. concentrated nitric acid to each beaker and evaporate carefully to 15 cc.; dilute with water and filter both solutions through an 11

cm. filter into a 250 cc. flask. Wash with water, heat to 85° C., add 40 cc. molybdate solution, and allow a current of air to bubble through the solution for five minutes to hasten the precipitation. Filter through a tared 9 cm. Munktell filter, previously dried at 110° C., and wash with 2 per cent. nitric acid until washings show no coloration, with potassium thiocyanate. Dry for thirty minutes at 110° C., and weigh as ammonium phosphomolybdate.

Determination of Manganese in Ores

Dissolve 1 gram in a 7½ cm. porcelain dish in 25 cc. concentrated hydrochloric acid, and evaporate to dryness. Redissolve in 25 cc. of 35 per cent. hydrochloric acid, boil gently, and filter into a No. 4 beaker. Burn the residue and fuse with eight times its weight of the mixed carbonates of potassium and sodium. Dissolve the fusion in hot water acidulated with hydrochloric acid, evaporate to dryness, redissolve as before, and filter into the beaker containing the original filtrate. Evaporate the solution to a small bulk, replace the evaporated water with nitric acid, evaporate again to a small bulk, add 60 cc. concentrated nitric acid, boil, and add potassium chlorate from time to time until the manganese is precipitated. Cool and filter through asbestos, with the aid of suction. Wash the manganese dioxide with colorless concentrated nitric acid and transfer the asbestos and precipitate to the beaker, which served for the precipitation. Wash the filtering tube with water and 50 per cent. hydrochloric acid. Add 25 cc. concentrated hydrochloric acid and a few drops of sulphuric acid to precipitate barium if present. Boil until the manganese is dissolved as chloride. Filter into a 500 cc. flask, wash three times with hot water, neutralize the solution with ammonia, add 10 cc. 25 per cent. ammonium acetate solution, boil, and filter into a 500 cc. flask. Dissolve the precipitate in dilute hydrochloric acid (in the flask in which the precipitation was made), make a second basic acetate precipitation, and filter into the flask containing the first acetate filtrate. Wash the flask and filter well with hot water. Add 10 cc. acetic acid, boil, and add 30 cc. saturated ammonium phosphate solution. Rotate the flask until the silky precipitate forms, add 25 cc. concentrated ammonia, shake until the precipitate is crystalline, and allow to settle. Filter through an 11 cm. filter-paper, wash with water, burn, and weigh as $Mn_2P_2O_7$.

Determination of Silicon in Pig Iron

Dissolve 1 gram of the sample in 20 cc. silicon mixture, heat gently for five minutes, and evaporate to dryness. Remove from the hot plate, cool, and redissolve in 20 cc. hot water and 5 cc. hydrochloric acid. Boil, and filter through an asbestos filter. Wash with cold water and hot 10 per cent. hydrochloric acid. Burn until white, and weigh as SiO_2.

Determination of Silicon in Steel

Weigh from 3 to 5 grams of the sample and use 20 cc. of the silicon mixture to each gram, after which proceed as in the case of pig iron.

Silicon Mixture.—Mix thoroughly 500 cc. concentrated nitric acid and 150 cc. concentrated sulphuric acid with 1500 cc. water.

Determination of Sulphur in Pig Iron and Steel

BY OXIDATION FOLLOWED BY PRECIPITATION AS BARIUM SULPHATE.

Dissolve 5 grams of the sample in a No. 6 beaker, with 45 cc. concentrated nitric acid and 5 cc. concentrated hydrochloric acid. When the violent action ceases evaporate to 10 cc., add 35 cc. concentrated hydrochloric acid to displace nitric acid, and boil to dryness on the steam-bath. Cool, add 35 cc. concentrated hydrochloric acid, evaporate until excess of hydrochloric acid is driven off; add 2 cc. concentrated hydrochloric acid, and dilute to 75 cc. with hot water. Filter into a No. 2 beaker, wash with cold water, add hot dilute hydrochloric acid, heat to 95° C., add 10 cc. 5 per cent. barium chloride solution, and evaporate almost to dryness. Redissolve in 2 cc. concentrated hydrochloric acid, dilute with cold water to about 200 cc., and set aside over night. Filter through a double 7 cm. Munktell No. 1 filter, wash with hot water and hot 5 per cent. hydrochloric acid until free from iron, burn until white, and weigh as $BaSO_4$.

EVOLUTION METHOD

Place 3 grams of the drillings into a 250 cc. ring-necked flask, provided with a doubly perforated stopper, in which is placed a safety funnel and a delivery tube, the upper end of which is bent twice at right angles and passes through the stopper into a 1 in.

by 10 in. test-tube. Into the latter is put 30 cc. of the zinc sulphate solution, and the evolution started by introducing 40 cc. of 50 per cent. hydrochloric acid through the funnel. Heat gently until the sample is dissolved and boil to expel the hydrogen sulphide. Disconnect and transfer the delivery tube and solution to a white bowl 4.5 in. by 4 in. Rinse both tubes into the bowl with water until the volume amounts to 200 cc. Now rinse the tubes with 20 cc. of 50 per cent. hydrochloric acid, add a little starch solution, and immediately titrate with standard iodine solution until a decided blue color appears.

SOLUTIONS

Iodine Solution.—Dissolve 4.8 grams resublimed iodine and 9 grams C. P. potassium iodide in 2.5 liters of water. Determine the value of the solution by the help of a standard steel in which the sulphur has been determined by oxidation.

Zinc Sulphate Solution.—Dissolve 200 grams zinc sulphate, C. P., in 1 liter of ammonia (sp. gr. 0.90), and dilute with water to 7 liters.

Starch Solution.—Stir 12.5 grams of arrowroot starch into water and bring to the consistency of cream. Pour into 1 liter of hot water and boil for ten minutes. To this solution add 12.5 grams C. P. zinc chloride dissolved in 1 liter of cold water. Allow the solution to stand over night and siphon the clear liquid into a bottle for use.

Determination of Phosphorus in Pig Iron

Place 2 grams of the sample into a 200 cc. beaker, add 75 cc. nitric acid (sp. gr. 1.13), and heat gently until the action ceases. Filter from the carbonaceous matter, oxidize the filtrate, and treat with a saturated solution of potassium permanganate exactly as in the case of steel.

Chilled pig iron is dissolved in nitric acid (sp. gr. 1.20) and the oxidation completed by evaporation to dryness and baking for one hour at a temperature of about 200° C. Redissolve in hydrochloric acid and replace with nitric acid. Make strongly ammoniacal and add concentrated nitric acid until the ferric hydroxide just dissolves. Cool or heat to 85° C. and add 40 cc. molybdate solution. Filter, wash with 1 per cent. solution of

nitric acid and 0.1 per cent. solution of potassium nitrate, and titrate. For check work and standards, I use Wood's chromic acid method and weigh the yellow precipitate; also the magnesia method as given in Lord's "Notes on Metallurgical Analysis," page 22.

Determination of Phosphorus in Steel

Place 2 grams of the sample into an 8 ounce Erlenmeyer flask, add 50 cc. nitric acid (sp. gr. 1.13), and heat until the drillings dissolve. Add from 5 to 10 cc. saturated potassium permanganate solution, according to the carbon content of the steel, boil until the potassium permanganate is decomposed, add from 1 to 2 drops of a saturated cane-sugar solution, then boil until the solution clarifies, and remove from the hot plate. Cool to about 50° C., add 5 cc. ammonia (sp. gr. 0.90) and rotate the flask until the ferric hydroxide dissolves. Insert a thermometer, cool or heat to 85° C., add 40 cc. molybdate solution, and agitate by a current of air for three minutes. Filter through a 7 cm. Munktell filter, using a cone and gentle suction; wash with 1 per cent. nitric acid solution, until free from iron, and finally with 0.1 per cent. potassium nitrate solution, to free from nitric acid. Allow the suction to dry the filter, remove from the cone, transfer to the carefully rinsed flask (which served for the precipitation), and add 25 cc. standard sodium hydroxide from an automatic pipette. Insert a rubber stopper, shake till the precipitate dissolves, wash down the flask and stopper with cold water, and add 3 drops of phenolphthalein solution. Titrate with standard nitric acid until the pink color is destroyed. The number of cubic centimeters of standard sodium hydroxide solution used in neutralizing the yellow precipitate represents the percentage of phosphorus.

SOLUTIONS

Molybdate Solution.—Dissolve 1 pound of molybdic acid in a mixture of 1200 cc. water and 700 cc. ammonia (sp. gr. 0.90), add 300 cc. nitric acid (sp. gr. 1.42), and pour the solution into a bottle containing 2 liters of nitric acid (sp. gr. 1.42) and 4.8 liters of water. Mix thoroughly and keep the solution for five hours before using.

Phenolphthalein Solution.—Dissolve 0.5 gram of phenolphthalein in 200 cc. of 95 per cent. alcohol.

Standard Nitric Acid Solution.—400 cc. of nitric acid (sp. gr. 1.42) are diluted in a 45 liter carboy to 40 liters.

Standard Sodium Hydroxide Solution.—308 grams C. P. sodium hydroxide are dissolved and diluted in a 45 liter carboy to 40 liters. This makes the standard approximately. Compare the strengths of the solutions and dilute to make them equal in value. Standardize with homogeneous steel in which the phosphorus has been determined gravimetrically.

Determination of Manganese in Steel and Pig Iron

GRAVIMETRIC METHOD

Digest 3 grams of the sample in a 200 cc. beaker in 50 cc. nitric acid (sp. gr. 1.20). Heat gently until all is dissolved, evaporate almost to dryness, add 75 cc. nitric acid (sp. gr. 1.42), boil, and add potassium chlorate until the manganese is oxidized, and finish as in the case of manganese in ores.

In case of high silicon iron, dissolve in 25 cc. concentrated hydrochloric acid, evaporate to dryness, and bake until free acid is expelled in order to render silica insoluble. Redissolve in hydrochloric acid, dilute, and filter. Evaporate the filtrate to a small bulk, repeat the evaporation twice with nitric acid, oxidize manganese with potassium chlorate and finish as in the case of manganese in steel and ores.

COLOR METHOD

Transfer the solution of the standard and test from the color carbon determination to 1 in. by 10 in. test-tubes, dilute to 25 cc. with water, boil, and (while boiling) add 0.5 gram lead dioxide from a small porcelain spoon and heat for two minutes. Remove the tubes from the flame, whirl in a centrifugal machine until the lead dioxide has deposited, cool, and compare as usual.

Pig Iron.—Weigh into 1 in. by 10 in. test-tubes 0.2 gram of the sample and standard, add 30 cc. nitric acid (sp. gr. 1.13), heat gently until all is in solution, boil, and (while boiling) add 0.5 gram of lead dioxide, and finish the same as manganese in steel.

Determination of Carbon by Combustion

Carbon is determined by Shimer's method as given in the *Journal of the American Chemical Society*, **21**, 557.

Determination of Tungsten in Steel

Dissolve 5 grams of drillings in 90 cc. nitric acid (sp. gr. 1.2), add 10 cc. concentrated sulphuric acid, and evaporate until copious fumes are given off. Cool, redissolve in 20 cc. concentrated hydrochloric acid and 50 cc. water, filter, and wash with hot 5 per cent. hydrochloric acid until the washings show no reaction with potassium thiocyanate. Ignite and weigh as $SiO_2 + WO_3$. Treat the residue with sulphuric acid and hydrofluoric acid, evaporate to dryness, ignite, and weigh again. The difference between the two weights is SiO_2. The residue contains 79.31 per cent. tungsten.

Determination of Nickel in Steel

Place 1 gram of drillings into a beaker of 150 cc. capacity, add 50 cc. of 20 per cent. sulphuric acid, cover, heat until all the steel is dissolved, evaporate to 35 cc., and cool in ice-water. Carefully add 50 per cent. ammonia until slightly ammoniacal. This point is indicated by the solution changing to a green color and a slight coating of iron oxide forming on the surface. Add 5 grams C. P. ammonium sulphate crystals and wash the cover and sides of the beaker with a jet of water. Heat to boiling and pass a current of hydrogen sulphide through the boiling solution for twenty minutes. Discontinue the hydrogen sulphide current, clean the tube, and wash the sides of the beaker, first with water and then, any sulphides still adhering, with a jet of hot 5 per cent. sulphuric acid, using as little as possible. Boil the solution, filter through a ribbed filter, and wash well with hot 5 per cent. ammonium sulphate solution and once with hot water. Transfer the filter and contents to a 250 cc. beaker, add 0.5 gram powdered potassium chlorate (C. P.), break the filter-paper, and mix thoroughly. Add 15 cc. concentrated hydrochloric acid, cover quickly and as soon as the action is over, stir well, add 15 cc. hot water and heat until all the nickel sulphide is decomposed. Filter and wash well with hot water, separate the iron in the filtrate with excess of ammonia, and filter. Acidulate the filtrate with hydrochloric acid, pass a current of hydrogen sulphide to precipitate any copper present, filter if necessary, and boil to expel hydrogen sulphide. In the meantime, dissolve the ferric hydroxide obtained, in dilute hydrochloric acid, reprecipitate, and filter.

Combine the two filtrates and make the solution as nearly neutral as possible. Heat to boiling and precipitate the nickel with 3 cc. of yellow ammonium sulphide. When all the nickel is precipitated, filter through an ashless filter, wash thoroughly with boiling water, dry, ignite in a porcelain crucible, and weigh as NiO.

Determination of Chromium in Steel

Treat 3 grams of the sample exactly as in the case of Ford's method for manganese, up to the filtration of manganese dioxide. Wash the manganese dioxide three times with cold water. Boil the filtrate to about 40 cc. to decompose the potassium chlorate. Dilute to 500 cc. with cold water and add standard ferrous sulphate solution until the green color of chromic nitrate appears. Add standard potassium permanganate solution till the excess of ferrous sulphate is oxidized as indicated by the typical pink color. The number of cubic centimeters of ferrous sulphate used to reduce the chromic acid, represents the percentage of chromium.

The Standard Ferrous Sulphate Solution is made by dissolving pure iron wire in an excess of dilute sulphuric acid, diluting with water until 1 cc. contains 0.003223 gram of iron in the ferrous condition.

The Standard Potassium Permanganate Solution is made by dissolving 1.818 grams of pure potassium permanganate in a liter of water. One cc. of the permanganate will then oxidize 1 cc. of the ferrous sulphate solution.

XVIII. Methods Used at the General Laboratory of the American Steel Hoop Company, Pittsburg, Pa.

By Henry S. Marsh

Determination of Iron in Iron Ores

One gram of the finely ground sample, previously dried at 100° C., is digested with hydrochloric acid (2:1) at a temperature below boiling until the insoluble matter becomes light and flocculent. Filter, and if the silicious matter contains iron, make a fusion and add the solution obtained to the main filtrate. Divide the filtrate into two equal portions, making up each portion to 75 cc., heat to boiling, and reduce the iron by dropping in stannous chloride solution till colorless, and then add 3 drops in excess. Cool the solutions and add, all at once, 15 cc. of a saturated solution of mercuric chloride. Titrate with a standard solution of potassium bichromate, 1 cc. of which equals 0.01 gram iron. The end of the reaction may be told by removing a drop of the solution to a dilute solution of potassium ferricyanide on a white porcelain plate. Toward the end of the reaction add 3 drops of the test and allow to stand for several minutes to make sure that oxidation is complete. The titrations on both portions should agree almost exactly. The sum of these represents the iron in 1 gram of ore.

SOLUTIONS

Potassium Dichromate Solution.—Dissolve 9.8 grams of the salt in 1 liter of water.

Stannous Chloride Solution.—Dissolve 100 grams of the salt in 1 liter of dilute hydrochloric acid (1:1).

Determination of Phosphorus in Ores

The finely divided sample is thoroughly dried and cooled in a

desiccator. 1.63 grams are weighed off into a casserole and dissolved in about 30 cc. of hydrochloric acid, the solution evaporated to dryness, 20 cc. of hydrochloric acid added, and the residue dissolved and evaporated to the first appearance of insoluble ferric chloride. A few drops of hydrochloric acid are added and the whole diluted with water to about 35 cc., and filtered. The operation after this stage is the same as described under pig iron.

Determination of Manganese in Ores

This determination is rarely called for. When necessary, the method of Volhard is used.

Determination of Silicon in Pig Iron

Dissolve 1 gram of the drillings by the aid of gentle heat in a small porcelain dish in 30 cc. of silicon mixture. Evaporate, after solution is complete, until a spongy mass is obtained. Cool, add 10 to 15 cc. concentrated hydrochloric acid, and evaporate rapidly to dryness. Take up with 10 cc. strong hydrochloric acid and 15 cc. water. Filter, wash thoroughly with water and a few drops of hydrochloric acid (1:1), and finally with hot water. Ignite until perfectly white. The weight of the silica, multiplied by 0.4667, equals Si.

The silicon mixture is prepared by mixing 1500 cc. water with 500 cc. nitric acid (sp. gr. 1.42), and 150 cc. sulphuric acid.

Determination of Phosphorus in Pig Iron

Dissolve 1.63 grams of the drillings in 50 cc. of nitric acid (sp. gr. 1.20) and evaporate the solution to hard dryness. The residue is then to be baked over a Bunsen burner flame. After cooling somewhat, add 15 cc. strong hydrochloric acid and evaporate to the first appearance of insoluble ferric chloride. Then add 3 or 4 cc. concentrated nitric acid and dilute to about 30 cc. with water; filter, washing with hot hydrochloric acid (1:1), and finally with hot water. In the case of pig iron containing 0.2 to 0.6 per cent. phosphorus, make up the filtrate to 100 cc. and take 50 cc. for the determination. In case of pig iron containing 0.6 per cent. or more of phosphorus, make up to 200 cc. and use 50 cc. for the determination. Neutralize the filtrate completely with ammonia and add concentrated nitric acid until the precipitate is dissolved and the solution is of a clear amber color. Heat to

80° C. and add 50 cc. molybdate solution, shaking for a few minutes. Allow to stand for twenty or thirty minutes and filter into a tared Gooch crucible, washing with 2 per cent. nitric acid. Dry at 100° C. for forty minutes and weigh. Each milligram represents 0.001 per cent. phosphorus in the sample.

Molybdate Solution.—100 grams molybdic acid are dissolved in a mixture of 265 cc. water and 155 cc. ammonia and 60 cc. concentrated nitric acid are then added. Filter and pour into a mixture of 440 cc. concentrated nitric acid and 1066 cc. water.

Determination of Sulphur in Pig Iron

GRAVIMETRIC METHOD

Dissolve 5 grams of the drillings in a casserole with 50 cc. concentrated nitric acid and add 10 cc. hydrochloric acid. After solution is complete add 0.5 gram potassium chlorate and 1 gram sodium carbonate, and evaporate to hard dryness. Take up in 20 cc. concentrated hydrochloric acid and again evaporate to dryness. Dissolve the residue in 25 cc. concentrated hydrochloric acid and evaporate to first appearance of insoluble ferric chloride. Add 5 cc. concentrated hydrochloric acid and boil till clear. Dilute with 25 cc. hot water and filter, washing with hot water and dilute hydrochloric acid. Make up the filtrate to 200 cc., bring to the boiling-point, and add 10 cc. of 10 per cent. barium chloride solution (stirring constantly). Allow to stand for five or six hours, and filter without suction, washing with hot water acidulated with a little hydrochloric acid. Ignite at a low red heat, after detaching the precipitate as well as possible from the filter-paper. Weigh as $BaSO_4$, containing 13.73 per cent. sulphur.

EVOLUTION METHOD

In the case of high sulphur pig irons weigh 2.5 grams, place in a flask provided with a tap-funnel and a delivery-tube connected, by a rubber hose, with a glass tube bent at an acute angle and reaching to the bottom of a 1 in. by 8 in. test-tube filled with ammoniacal cadmium chloride solution. Two bulbs are blown on the ascending short arm of the delivery tube to catch any acid which might distil over into the absorption tube. Fifty cc. of dilute hydrochloric acid (1:1) are introduced into the flask and heat applied to produce a fairly rapid evolution of gas. When

the sample is completely dissolved, the heat is raised and the solution boiled for a few minutes to expel all hydrogen sulphide, after which the absorption tube is detached. The contents are poured slowly, care being taken not to disturb the heavy yellow particles at the bottom, into a beaker containing 200 cc. cold water. The tube is washed with a little dilute hydrochloric acid (1:1), filled with cold water, and emptied into the beaker. This is repeated once, the delivery tube being also washed into the beaker. Add an excess of dilute hydrochloric acid (1:1) to the liquid and 4 or 5 cc. of starch solution. Titrate with iodine solution, each cubic centimeter of which represents 0.01 per cent. sulphur, using a 5 gram sample. A blank test should be made occasionally to determine the amount of iodine used by the reagents, and a proper deduction made.

SOLUTIONS

Iodine Solution.—Four grams iodine are dissolved in a solution of 8 grams of potassium iodide in 10 cc. water and the solution is made up to 1 liter. Standardize by the bichromate and thiosulphate method.

Cadmium Chloride Solution.—Twenty-five grams cadmium chloride are dissolved in 250 cc. water and 125 cc. ammonia. Then add 500 cc. water and make up to 2 liters with ammonia.

Starch Solution.—Five grams starch are made into a paste with a few cubic centimeters of water and poured into 1 liter of boiling water, after which 6.6 grams zinc chloride are added. Allow to stand over night and use the clear decanted liquid.

Determination of Manganese in Ferromanganese

Dissolve 1 gram of the metal in 40 cc. nitric acid (sp. gr. 1.20), pour into a liter flask, add an excess of zinc oxide stirred up in water, and make up to 1 liter. Pour into a dry beaker and mix thoroughly. After settling, decant 200 cc. into a flask, make up to 400 cc., and titrate boiling hot with potassium permanganate. The permanganate solution contains 3.5 grams of the salt in 1 liter of water.

Determination of Manganese in Ferrosilicon and Silicospiegel

Two grams of the metal, pulverized so as to pass through a sieve of 20 meshes to the inch, are dissolved in dilute nitric acid. The solution is poured into a liter flask, zinc oxide added, and

the volume made up to 1 liter. After subsidence, 500 cc. are poured off and titrated at the boiling-point with potassium permanganate.

Determination of Silicon in Ferrosilicon and Silicospiegel

One-half gram of sample, pulverized to pass through a 120 mesh sieve, is dissolved in dilute hydrochloric acid (3:1), with a few drops of nitric acid and evaporate to dryness. Take up the residue in 25 cc. strong hydrochloric acid and evaporate rapidly to dryness. Dissolve in 25 cc. strong hydrochloric acid and evaporate to first appearance of insoluble ferric chloride. Add 4 or 5 cc. hydrochloric acid and, when dissolved, dilute with 30 cc. water. Filter and wash with water and hot dilute hydrochloric acid alternately and finally with hot water. Ignite and weigh in the usual manner. Silicon factor, 0.4667.

Determination of Silicon in Steel

Three grams of steel are dissolved in 30 cc. concentrated hydrochloric acid and 3 or 4 cc. nitric acid and evaporated quickly to hard dryness; it is then taken up in 20 cc. concentrated hydrochloric acid and evaporated quickly to the first appearance of insoluble ferric chloride. Three or four cc. strong hydrochloric acid are added and the solution boiled until clear. The solution is diluted with 25 cc. water and filtered through ashless filter-paper. Ignite until perfectly white, and weigh. 0.4667 of this is silicon.

Determination of Phosphorus in Steel

1.63 grams of drillings are dissolved in 50 cc. nitric acid (sp. gr. 1.20), an excess of a solution of potassium permanganate is added and the whole boiled for three minutes. The precipitate is dissolved in a small quantity of hydrochloric acid and the solution evaporated to 20 cc. Dilute with water to 50 cc. and neutralize with ammonia water. Add nitric acid until the solution is of a cletar amber color. Heat to 80° C. and add 50 cc. molybdate solution. Shake well, allow to stand twenty or thirty minutes, and filter into a Gooch crucible. Dry at 100° C. for forty minutes and weigh. Each milligram of precipitate corresponds to 0.001 per cent. phosphorus.

Determination of Sulphur in Steel

The evolution method is used as described under pig iron.

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Determination of Manganese in Steel

COLOR METHOD

Two-tenths gram of the sample is dissolved in a mixture of 5 cc. water and 16 cc. of nitric acid (sp. gr. 1.20) in a 100 cc. flask. After solution, make up to 40 cc. and heat to boiling. At the same time an equal weight of a standard steel is treated in exactly the same manner. Add 0.5 gram lead peroxide to each portion and boil for three minutes. Pour off into tubes and allow to stand in water until cold. The excess of lead peroxide is then caused to subside completely by the use of a centrifugal machine and the solutions are then compared as to color.

Determination of Nickel in Steel

Two grams of drillings are dissolved in 35 cc. strong hydrochloric acid and 1 cc. nitric acid and evaporated to 10 cc. Transfer to a 250 cc. separatory funnel and use as little warm hydrochloric acid (2:1) as possible in rinsing into the funnel. Cool and add 40 cc. pure ether which has been previously agitated with 5 cc. hydrochloric acid. Shake vigorously, cooling from time to time. Allow to stand and run off the aqueous solution. Wash the ether by shaking with two lots of 5 cc. each of hydrochloric acid (sp. gr. 1.13). Boil out the ether, precipitate the iron with ammonia, adding a little bromine water to precipitate the manganese. Evaporate the excess of ammonia, obtaining a solution of 100 cc. containing 1 cc. ammonia. Precipitate the nickel by hydrogen sulphide, filter, and weigh as NiS containing 0.7855 nickel.

Determination of Chromium in Steel

Three grams of the drillings are dissolved in 50 cc. strong hydrochloric acid and the solution evaporated to a moist cake. Add 50 cc. strong nitric acid and boil to expel nitrous fumes. Add 4 grams of potassium chlorate and evaporate to 30 cc. Dilute to 300 cc., add 15 cc. of ammonia water, mix well, and filter, when cold. Dilute the filtrate and washings to 450 cc., and add a slight excess (accurately measured) of a standard solution of ferrous ammonium sulphate. The excess of the ferrous salt is then determined by titration with potassium permanganate. Unless the solution is dilute, the filter-paper may cause partial reduction of the chromic acid. The proportion of the chromium is then calculated.

XIX. Methods Used at the Laboratory of the American Steel and Wire Company, Shoenberger Steel Works, Pittsburg, Pa.

By G. D. Chamberlain

Determination of Silica in Ores

One-half gram of the ore is mixed in a platinum crucible with ten times its weight of mixed sodium and potassium carbonates, and fused over a blast-lamp for from ten to twenty minutes, or until a clear fusion results. Pour the contents of the crucible into a platinum dish kept floating on water. The fused cake is placed in 150 cc. of hydrochloric acid (sp. gr. 1.1) and the portion of the fusion adhering to the crucible dissolved in the same liquid. The solution is evaporated to dryness, taken up with 50 cc. of hydrochloric acid, diluted and filtered, and the silica burned and weighed in the usual manner.

Determination of Iron in Ores

The Zimmerman-Reinhardt method is used, as described by Mixer and Dubois.[1]

From ½ to 1 gram of the finely ground ore is placed in a No. 0 or 00 lipless beaker, 10 to 15 cc. of strong hydrochloric acid are added and the beaker heated on a steam-bath over night, or until the ore is decomposed, and the solution concentrated to about 4 to 6 cc. Reduce wth stannous chloride solution, using a weaker solution to complete the reduction, and taking care to avoid an excess of more than 3 or 4 drops. The moment of complete reduction can be readily observed if the beaker is placed on a white surface. Dilute to 350 or 400 cc., add 5 cc. of mercuric chloride solution, then 25 cc. of titrating solution, and titrate promptly with standard permanganate. The solution of the ore may be hastened by adding stannous chloride (less than enough

[1] Eng. and Min. J., April 14, 1894.

to effect complete reduction of the iron to the ferrous condition) with the hydrochloric acid. The permanganate solution is standardized with one or more ores in which the iron has been accurately determined, although the use of iron wire gives concordant results. A standard ore is run in duplicate with each batch of ores. While this is not absolutely necessary if the quantities of reagents used are kept uniform, it requires little time and serves as a convenient method of checking the method and manipulations.

The important point in using the method is to avoid a large excess of the stannous chloride and to keep this excess as nearly constant as possible in all determinations. The results are accurate and the process requires less time than the ordinary bichromate method.

SOLUTIONS

Stannous Chloride Solution.—One pound of the salt is dissolved in 500 cc. of concentrated hydrochloric acid and the solution diluted to 2250 cc. For finishing the reduction a portion of this solution is diluted with three or four times its bulk of water. The addition to the ore solution is made by means of a dropping tube or burette.

Mercuric Chloride Solution.—This contains 5 per cent. of the salt.

Titrating Solution.—160 grams of manganese sulphate are dissolved in water and made up to 1750 cc. 350 cc. each of sulphuric acid and sirupy phosphoric acid are then added.

Potassium Permanganate Solution.—This contains 3.5 grams of the salt in 1 liter, and is accurately standardized.

Determination of Aluminum in Ores

Aluminum is determined in the filtrate from the silica by Peters' modificaton of Woehler's method.[1] In the case of manganese ores or of iron ores containing much manganese, one or two basic acetate separations must be made.

Determination of Phosphorus in Ores

From 2 to 5 grams of the ore are dissolved in 30 to 60 cc. of concentrated hydrochloric acid, the solution is evaporated to dry-

[1] Blair's "Chemical Analysis of Iron," third edition, p. 250.

ness, and the residue taken up with 15 to 30 cc. of hydrochloric acid. The solution is filtered into a 250 or 500 cc. Erlenmeyer flask, washing the residue twice with hydrochloric acid (sp. gr. 1.10) and water. Evaporate to a sirupy consistency, and add 20 to 30 cc. concentrated nitric acid. Boil to remove hydrochloric acid, concentrating to about 10 to 15 cc. The residue is fused with mixed carbonates, dissolved in hydrochloric acid (sp. gr. 1.10), and evaporated to dryness. Just enough of the same acid is added to moisten the residue (5 to 8 cc.). Place on the steam-bath for fifteen minutes, add water to make up to about 40 to 60 cc. boil and filter into the flask containing the main solution, washing well with water and hydrochloric acid. The volume of the solution should now be about 75 to 100 cc. A slight excess of concentrated ammonia water is added and nitric acid sufficient to redissolve the precipitate. The solution is warmed to 85° C., and 50 cc. of molybdate solution added. After shaking for five minutes the yellow precipitate is filtered off and in the case of routine work the phosphorus is determined by Handy's volumetric method.[1]

When it is found necessary to check results, the phosphoric acid of the yellow precipitate is converted into ammonium magnesium phosphate and the phosphorus finally weighed as magnesium pyrophosphate.

Molybdate Solution.—Three-fourths of a pound of molybdic acid is made up into a paste with 900 cc. of water. 525 cc. of ammonia water are then added to dissolve the molybdic acid. 250 cc. of concentrated nitric acid are added to partially neutralize the ammonia (if this is not done precipitation occurs on adding to nitric acid). After cooling, partially filter or pour the solution into a 2 gallon bottle containing 3600 cc. of water and 1500 cc. of concentrated nitric acid, through which a current of air is being blown in order to mix and cool the solution. This solution may be kept for long periods.

Determination of Manganese in Ores

Volhard's method is employed, using 1 or 2 grams of the ore and testing the insoluble residue for manganese. The iron is precipitated by zinc oxide, and, without filtering, the solution

[1] *Proceedings of the Chemical Section, Engineers' Society of Western Penna.*, March 11, 1892.

is boiled and the manganese titrated in presence of the precipitated ferric hydroxide. This does not interfere with the titration but seems rather to facilitate the recognition of the end-point, by causing the solution to become rapidly clarified.

In the case of manganese ores and for the purpose of checking results, Ford's method is used as described by C. B. Murray.

Determination of Nickel in Steel

The nickel is separated from the iron in hydrochloric acid solution by means of ether and finally weighed as NiO, according to the method described by Chase.[1]

Determination of Manganese in Ferromanganese

Volhard's method is used, standardizing the permanganate solution by means of a ferromanganese sample, in which the proportion of manganese has been accurately determined by a gravimetric method. Manganese is determined gravimetrically as a check in special cases.

[1] Blair's "Chemical Analysis of Iron," third edition, appendix.

XX. Methods Used at the Laboratory of the Pittsburg Steel Foundry Company, Glassport, Pa.

By George E. Hodge

Determination of Silica in Ores

Five grams of the agate mortar sample, dried at 100° C. for one hour, are treated in a 12 cm. covered porcelain dish with 50 cc. concentrated hydrochloric acid and the dish allowed to go to dryness over night on the sand-bath.

Thirty cc. concentrated hydrochloric acid are then added, the dish is warmed and the solution evaporated till ferric chloride begins to separate, when this is redissolved with a few drops of hydrochloric acid, the solution diluted to 75 cc. with hot water, and filtered through a 9 cm. filter into a 500 cc. flask.

The residue is ignited, fused with from 3 to 5 grams of mixed carbonates, the fusion dissolved in hot water, the solution acidified with hydrochloric acid and evaporated to dryness, moistened with dilute (1:2) hydrochloric acid, diluted with hot water, and filtered into a flask containing the first filtrate, washing with hot (10 per cent.) hydrochloric acid. The residue is burned and weighed as silica.

Determination of Iron in Iron Ores

One gram of the steam-dried sample is placed into a No. 0 beaker provided with a glass cover and treated with 3 cc. stannous chloride solution and 25 cc. hydrochloric acid, and heated till all is dissolved but the insoluble silicious residue. Stannous chloride solution is then added until the color due to ferric chloride is destroyed and then one drop in excess.

The solution, contained in a No. 5 beaker, is diluted with 300 cc. cold boiled water and while stirring 10 cc. mercuric chloride solution are added. After standing one minute, standard potassium dichromate is run in from a burette until a drop of the solution

fails to give a green color with a drop of potassium ferricyanide on a test-plate. The number of cubic centimeters used equals the percentage of iron.

SOLUTIONS

Stannous Chloride Solution.—150 grams stannous chloride are dissolved in 250 cc. hydrochloric acid and 250 cc. water. 1 cc. will reduce 0.1 gram iron.

Mercuric Chloride Solution.—25 grams of the salt are dissolved in 500 cc. water.

Potassium Ferricyanide Solution.—A small crystal is dissolved in 25 cc. water.

Standard Potassium Bichromate Solution.—30 grams of the salt are dissolved in water; the solution is made up to 3.5 liters and standardized with ferrous ammonium sulphate.

Determination of Phosphorus in Ores

The united filtrates from the silica obtained in the determination of that constituent, and which should not exceed 150 cc. in volume, are evaporated to about 75 cc., nitric acid is added and the evaporation continued until hydrochloric acid is driven off.

Ammonia is now added in slight excess, then nitric acid in slight excess, and the solution brought to 60° or 70° C., 50 cc. molybdate solution are added and the flask shaken five minutes by a machine. The precipitate is treated as in the case of a steel.

For the preparation of the solutions, see the method for pig iron and steel, page 136.

Determination of Manganese in Ores

This element is determined gravimetrically by the method of J. M. Camp, page 38.

Determination of Silicon in Steel, Pig Iron, Ferrosilicon, Etc.

Three grams of steel, or 1 gram of pig iron, are weighed into a 6.5 cm. porcelain dish, provided with a glass cover and 50 cc. concentrated hydrochloric acid added. The solution is then evaporated to dryness and baked over an Argand burner until the residue is brown.

The dish is then cooled and the residue taken up in 25 cc. hydrochloric acid, and the solution evaporated just to dryness when the dish is again cooled and 15 cc. concentrated hydrochloric acid

and 75 cc. hot water added and the dish heated till the ferric chloride is in solution.

The insoluble matter is then caught on a 9 cm. Munktell filter over a pump, well washed with hot hydrochloric acid (1:3), ignited over the blast-lamp and weighed.

To the crucible 3 drops sulphuric acid and 15 drops hydrofluoric acid are added. After evaporating, the residue is ignited again and weighed. The loss in weight $\times$ 0.4702 = silicon.

In the case of ferrosilicons use 0.5 gram and treat with 75 cc. of a mixture made up of 150 cc. sulphuric acid (1:3), 150 cc. hydrochloric acid (1.20 sp. gr.), and 500 cc. water. After solution, evaporate to dryness. Fifteen cc. concentrated hydrochloric acid and 50 cc. hot water are then aded, the mixture warmed and the silica collected on a 9 cm. filter, burned and weighed. Treat with sulphuric and hydrofluoric acids, evaporate, ignite, and weigh. The loss in weight $\times$ 0.4702 = silicon.

Determination of Sulphur in Pig Iron and Steel

GRAVIMETRIC METHOD

Five grams of the sample are placed into a deep 15 cm. dish and treated with 40 cc. aqua regia (36 cc. concentrated nitric acid to 4 cc. concentrated hydrochloric acid).

Heat is applied when the violent action ceases and the solution is evaporated to one-half the original volume when 50 cc. concentrated hydrochloric acid are added and the solution (still under glass) allowed to go slowly to dryness on the sand-bath.

Forty cc. concentrated hydrochloric acid are now added and the beaker warmed until all is in solution when evaporation is continued until excess of hydrochloric acid is driven off.

A few drops of hydrochloric acid and about 75 cc. water are then added, the dish warmed and the insoluble residue caught on a 9 cm. filter, washing with hot 10 per cent. hydrochloric acid.

The filtrate in a No. 2 beaker is heated to incipient boiling, 15 cc. of 10 per cent. barium chloride solution added, and the excess of hydrochloric acid removed by evaporating to a sirup.

A few drops of hydrochloric acid are now added and 100 cc. hot water, and then, after standing for a few minutes, the beaker is placed into cold water.

Next morning the precipitate is collected on a 5 cm. filter,

washed with 10 per cent. hydrochloric acid, burned in an open crucible, and weighed as barium sulphate.

EVOLUTION METHOD

Five grams of the sample are weighed into a 500 cc. Erlenmeyer flask provided with a rubber stopper carrying a funnel and delivery tube. The latter tube passes to within 6 mm. of the bottom of a soda-water glass containing 25 cc. cadmium chloride solution and 300 cc. water.

Seventy-five cc. warm dilute hydrochloric acid (1:2) are admitted through the funnel tube and a gentle heat applied to the flask until solution is effected, when the heat is increased so that steam just washes the delivery tube.

After disconnecting the delivery tube, the source of heat is removed, 5 cc. starch solution and 25 cc. hydrochloric acid added to the contents of the soda-glass, and standard iodine solution run in from a burette, maintaining a blue color till the cadmium sulphide is dissolved, and the color remains permanent for two minutes.

SOLUTIONS

Cadmium Chloride Solution.—Thirty-one grams of the salt are dissolved in 300 cc. water, 160 cc. ammonia water (sp. gr. 0.90) added, then 625 cc. water and finally ammonia water (sp. gr. 0.90) to fill a 2.5 liter bottle. The solution is then filtered.

Starch Solution.—Ten grams of wheat starch, made to a thin paste with cold water in a mortar, are added to 1 liter of boiling water, boiled five minutes, and 50 cc. of a 10 per cent. solution of zinc chloride, slightly acidified with hydrochoric acid, added.

Iodine Solution.—Twenty-five grams of iodine are dissolved with 70 grams of potassium iodide in 50 cc. water and the solution so diluted that 1 cc. corresponds to 0.005 per cent. sulphur when 5 grams of steel are used in a determination.

Determination of Phosphorus in Pig Iron and Steel

In the practice at this laboratory a rapid method is usually required. Two grams of the steel drillings are weighed into a 500 cc. wide-mouthed Erlenmeyer flask, 100 cc. boiling dilute nitric acid (sp. gr. 1.135) added, and the flask heated strongly over an Argand burner until the steel is in solution and nitrous fumes are driven off. Ten cc. potassium permanganate solution are

then added and the boiling continued two minutes, or until the permanganate color is destroyed. While still at the boiling-point, 10 cc. ferrous sulphate solution are added and the flask removed from the heat after one minute, or when nitrous fumes are no longer evolved. Forty-five cc. dilute ammonia (sp. gr. 0.96) are added without waiting for the solution to cool. The solution is now quickly cooled to 60° or 70° C. and 50 cc. molybdate solution added.

After shaking by machine for three minutes the precipitate is caught on a 9 cm. filter (using suction), washed well with 2 per cent. potassium nitrate solution (fifteen times) and with the filter thrown into a beaker containing 10 to 25 cc. standard potassium hydroxide solution and 50 cc. of water, the whole having been previously heated to boiling.

The filter is stirred about to hasten the solution of the precipitate and after two minutes 1 drop of phenolphthalein is added and the hot solution titrated with standard nitric acid until colorless and then with standard potassium hydroxide until faintly pink.

(cc. KOH — cc. HNO_3) $\times$ 0.0050 = per cent. phosphorus.

With pig iron the silica, etc., is caught on a filter before the addition of the molybdate solution. Otherwise the operation is the same.

SOLUTIONS

Potassium Permanganate Solution.—Dissolve 15 grams of the salt in 1 liter of water.

Ferrous Sulphate Solution.—A saturated solution with 5 cc. sulphuric acid to the liter is used.

Molybdate Solution.—This is prepared according to Blair ("Chemical Analysis of Iron." third edition, p. 99).

Standard Potassium Hydroxide Solution.—Thirty-two grams of stick potash, as free from carbonate as possible, are dissolved in water and made up to 6 liters with cold boiled water and so diluted that 1 cc. equals 0.005 per cent. phosphorus, when 2 grams of steel are used.

Standard Nitric Acid.—One cc. equals 1 cc. potassium hydroxide solution. The potash solution is standardized by using a steel of known phosphorus content and also by means of ores in which the phosphorus has been determined gravimetrically.

Determination of Carbon and of Manganese in Steel by Color Methods

One-half gram of the steel sample and an equal weight of the standard are weighed and placed into large test-tubes and boiled with 10 cc. of nitric acid (sp. gr. 1.20) until all is dissolved.

The tubes are now allowed to cool and the carbon determined by comparison. The solutions are poured from the comparison tubes into 100 cc. cylinders, the tubes rinsed once and the volume of the solutions made up to 100 cc.

After mixing thoroughly, a 10 cc. pipette is rinsed with 10 cc. of the solution of the standard, then 10 cc. of the same solution are drawn up into the pipette and placed into a test-tube, 2.5 cm. wide and 20 cm. deep, and 10 cc. of nitric acid (sp. gr. 1.20) drawn through the pipette to rinse it, the rinsings being added to the solution in the test-tube.

Both of the samples are treated in the same way and the lot heated to boiling over a burner. A little amorphous silica is then added to prevent bumping, and while boiling a half gram of lead peroxide is cautiously dropped into the solution. After boiling three minutes, the rack is set in the dark to cool and the batch compared after standing twenty minutes.

The solution of the standard is diluted so that 1 cc. corresponds to 0.02 per cent. manganese on 0.5 gram of steel.

Determination of Nickel in Steel

ETHER METHOD

Dissolve 2 grams of steel drillings in 40 cc. hydrochloric acid, then add 3 cc. nitric acid (sp. gr. 1.20), and evaporate to about 20 cc. Transfer to a separatory funnel, rinsing out the flask with hydrochloric acid (sp. gr. 1.135). Keep the bulk of the solution down to 40 cc. Then add an equal volume of ether, shake, allow to settle a few moments, and draw off the bottom layer of the solution. Heat until all ether is driven off and then make two ammonia precipitations to separate the iron. Neutralize the blue solution with acetic acid, render slightly ammoniacal again, and precipitate with hydrogen sulphide. Acidify with acetic acid, boil a few minutes, filter, ignite, and weigh as NiO. Or, the nickel may be determined volumetrically as follows:

Proceed as above until the blue nickel solution is obtained, then neutralize with hydrochloric acid and cool, render slightly ammo-

niacal, add 5 cc. potassium iodide and 5 cc. silver nitrate, and titrate with a standard solution of potassium cyanide.

SOLUTIONS

Potassium Iodide Solution.—Dissolve 20 grams of the salt in 1 liter of water.

Silver Nitrate Solution.—Dissolve 0.5 gram of the salt in 1 liter of water.

Potassium Cyanide Solution.—Dissolve 4.65 grams of the salt in 1 liter of water and standardize by means of a steel of known nickel content.

Determination of Chromium in Steel and Iron Ores

The method of A. G. McKenna, page 152, is used.

Determination of Carbon in Steel

The method described by Blair, "Chemical Analysis of Iron," third edition, page 148, is used.

APPENDIX

The Determination of Phosphorus in Coke and Coal

By J. M. Camp[1]

One of the requirements at the laboratory of which the writer has charge, is the determination of the ash, sulphur and phosphorus, each day in an average sample of coke of the previous day's charge at all furnaces. The fusion of the ash, consisting of about 50 per cent. silica, 30 per cent. alumina and 10 per cent. iron sesquioxide with other bases, and the final evaporation to dryness to separate silica, is at best a tedious process which can not be safely hastened. The result is that the time required for the analysis is inconveniently prolonged, and consequently the following improved method has been successfully used, yielding excellent results and occupying much less time.

The sample of coke partly dried and ground to pass through a 40 mesh sieve is delivered at the laboratory by the sampler on the afternoon of the day of which it was taken. This is dried at 100° C. for one hour, and, when cool, 5 grams are weighed off into a porcelain crucible 1.75 inches in width. The crucible is left in the muffle furnace over night, and in the morning the mass of ash and any particles adhering to the crucible, are transferred to a 30 cc. platinum crucible mounted on a platinum tripod. About 5 cc. of dilute hydrochloric acid are now added (1 part acid, 2 parts water), and about 10 cc. of hydrofluoric acid, and the crucible and tripod are placed directly on the top of the chimney of an Argand burner and the flame so regulated that the solution will not boil. In from twenty to thirty minutes the solution is evaporated. The residue is heated to drive off the last traces of hydrofluoric acid, but not baked, as this would render some of the bases insoluble in the dilute acid to be subsequently used. When cool, about 15 cc. of the same dilute hydrochloric acid are added and the crucible warmed until all is in solution. The contents of the crucible are now transferred to a 12 cm.

[1] *Iron Age*, **65**, 17.

evaporating dish and 5 cc. of strong nitric acid added. The solution now amounts to about 75 cc. It is boiled for one or two minutes and then filtered, to remove any possible traces of silica or unconsumed carbon, into a 16 ounce flask.

Twenty-five cc. of strong ammonia are then added, then strong nitric acid until the precipitated iron and alumina are just dissolved, and 5 cc. in excess, making a total of about 25 cc. strong nitric acid.[1]

The solution is brought to 85° C. and 75 cc. of molybdate solution introduced by aid of a pipette, after which the solution is kept agitated for about five minutes, and is then filtered through a weighed filter-paper that has been dried at 115° to 130° C., and weighed between watch-glasses. The precipitate is washed with a 2 per cent. solution of strong nitric acid, dried one hour at the above temperature and weighed between watch-glasses. 1.63 per cent. of its weight is taken for phosphorus.

In the case of coals the treatment is exactly similar, except that the coal is usually coked in a large platinum crucible and then, to save the platinum crucible from the protracted heating, the coke is transferred to a porcelain crucible for complete combustion in the muffle preferably over night.

[1] *Proc. Eng. Soc. W. Pa.*, 11, 251.

The Determination of Phosphorus in Ores, Pig Iron and Steel Containing Arsenic

By J. M. Camp[1]

For the exact determination of phosphorus in ores, particularly in manganese ores, coming as they do from all quarters of the globe, and in pig iron or steel containing arsenic, a method is very desirable whereby at some stage of the analysis the arsenic can be eliminated without a marked change in the essential details of the regular phosphorus determination and without prolonging the time of the analysis. Numerous experiments have been made by the writer mainly in the attempt to reduce the concentrated ferric chloride solution to the ferrous state, and then volatilize the resulting arsenious chloride, but without success, until, acting on the suggestion contained in the paper by Mr. E. D. Campbell[2] describing briefly some experiments made by his students who used oxalic acid as a reducing agent, the following scheme was worked out. Excellent results were obtained with as much as 1 per cent. of arsenic. The method for ores only will be given; its application to steel and pig iron will be readily understood.

Five grams of the ground and dried sample are weighed off into a 12 cm. porcelain dish with a watch-glass cover, and 50 cc. strong hydrochloric acid added. The solution is boiled gently for about thirty minutes. It is now diluted with sufficient cold water to prevent corrosion of filter-paper and filtered into another dish of the same size. This solution will contain all the unvolatilized arsenic in the ore. It is placed on the steam-bath to go to dryness over night. The residue is burned and fused with the mixed carbonates and the fusion is allowed to harden around a platinum rod. The crucible is now warmed, and the fused mass removed on the platinum rod. This, while still hot, is placed into the dish, with a cover, in which the ore was originally dissolved and containing 10 or 15 cc. of water. Dilute hydrochloric

[1] *Iron Age*, **65**, 17.
[2] *J. Anal. Appl. Chem.*, **7**, 2.

acid is added and the crucible is warmed. This process is repeated until all its contents are removed, and they are then added to the dish containing the fusion. An excess of strong hydrochloric acid is now added to dissolve any of the remaining fusion, and this dish is placed with the other on the sand-bath. In the morning, to the dish containing the dried mass from the original filtrate, 2 grams of pure oxalic acid are added and 50 cc. of strong hydrochloric acid, and the solution, with a watch-glass cover, evaporated to dryness by hard boiling, but not baked. When cool add 30 cc. strong hydrochloric acid and evaporate to first appearance of insoluble ferric chloride, remove from the heat and add 10 cc. strong nitric acid. When the violent action has ceased warm until all is in solution, dilute with cold water and filter into a 16 oz. flask, using 2 per cent. nitric acid for washing. In the meantime, to the dish containing the fusion, dilute hydrochloric acid is added just sufficient to moisten, and enough hot water to dissolve the chlorides. This is warmed until all is in solution but the separated silica, and filtered into the same flask with the original filtrate. The phosphorus is now precipitated as above described for phosphorus in coke.

The Determination of Alumina as Phosphate in Ore and Blast-Furnace Cinder

By J. M. Camp[1]

The greatest advantages which precipitating and weighing alumina as phosphate has over the hydrate precipitation is in ore analysis, where, with the latter method, the iron and alumina are weighed together, the iron being finally determined by solution of the precipitate and titration, or preferably titration in another portion of the same sample. All the errors of the entire manipulation are thus thrown on the alumina. In the phosphate precipitation, however, the alumina is determined in a separate portion, and is responsible only for its own manipulative errors. In the case of blast-furnace cinders, the determination of the alumina, is the daily task of the laboratory, but the determination of iron is entirely omitted. Most furnace managers are content to receive the silica and alumina in each day's cinders, counting the balance as bases, with a full analysis at regular stated intervals. The iron not being an essential component of the cinder, its determination in a cinder of a normally working furnace, where it is little more than a trace, is useless, while with an abnormally working furnace where it may be high, the manager has something else on hand to worry him, of much more importance.

The filtration and washing of the phosphate precipitate are also much more rapid than the same operations with the hydrate precipitate; this statement applies particularly to cinders, where the large amount of alumina apparently coagulates the separated sulphur and the precipitate settles rapidly, leaving the supernatant liquid practically clear and readily decanted. In ores where there is much less alumina, more free sulphur is in suspension and a partial but not serious clogging of the filter occurs.

One disadvantage of the phosphate method is that there is no end-point to the washing of the precipitate, it being slightly soluble in the wash-water, and after the tenth washing showing with molybdate solution a fairly uniform volume of phospho-

[1] *Iron Age*, **65**, 17.

molybdate precipitate in equal volumes of the successive filtrates up to the twentieth washing. The addition of acetic acid and ammonium acetate to the wash-water gave a slightly greater weight of aluminum phosphate from a slag of known composition, but still showed the phosphate in the filtrates up to the twentieth washing. It is important that the precipitate be washed thoroughly; otherwise the platinum ware, if used, will suffer.

The method as used for ore and cinders is as follows:

To the cold hydrochloric acid filtrate from the silica of 1 gram of ore or cinder, diluted to about 400 cc. in a No. 5 beaker, add 30 cc. of a 10 per cent. solution of ammonium phosphate and then ammonia until a faint permanent precipitate is formed. One and a half cc. of strong hydrochloric acid are now added, and for ores, on account of the greater proportion of iron present, 50 cc. of a 20 per cent. solution of sodium thiosulphate are added. For cinders 30 cc. are sufficient. The beaker is now placed over a flame and heated just to boiling. In the same graduate, measure off 8 cc. of strong acetic acid, and 15 cc. of a 20 per cent. solution of ammonium acetate solution, and add to the solution which is maintained at the boiling-point for ten minutes. If this addition is made before the boiling-point is reached the precipitate will be flocculent and difficult to filter. Remove the beaker from the heat and allow the precipitate to subside; decant the clear solution, bring the precipitate upon the filter, and wash ten times with hot water. Transfer the precipitate to a platinum crucible without a lid and place in the front part of the muffle. When the paper is charred expose the crucible to the highest temperature of the muffle until white. Cool and weigh. 41.85 per cent. of the weight is alumina.

Blast-Furnace Cinders and Their Analysis

By J. M. Camp

It is the object of this paper to deal exclusively with the cinder made in furnaces making Bessemer iron, for the reason that that iron is almost exclusively the product of the furnaces of this region, the largest producers and consumers of the world being found here; and also for the reason that the writer's experience has been particularly confined to that field. On account of the easy solubility of cinders, and the simplicity of the analysis in general, this paper is dedicated to those who know nothing of the subject. In it they will find much that is old and, possibly, some few things that are new.

In the analysis of cinder, as in many other cases, it is of prime importance that the results, to be of service to the furnace manager, be obtained quickly. Consequently, the methods used are those yielding the quickest results with the maximum accuracy, the trifling errors, due to the rapid manipulation, being offset by variations in each cinder flush, and variations from flush to flush. Such differences are due to several causes, chief among which are the following:

First. Changes in the burden, due to variations in the weights of ore or flux. *Second.* Variations, more or less great, in the ore, flux, or fuel, which the method or time of sampling will not show. *Third.* Most important, and ever-varying changes, due to the reduction of more or less silica to silicon in the hearth, and its consequent absorption by the iron and loss to the cinder. This latter change is due to the variation in the temperature of the hearth, and may be caused by: (1) A reduction of the burden; (2) Extra coke, or, as is commonly called, a blank charge; (3) To a higher or lower temperature of blast; (4) A slip in the furnace with the resulting introduction of cold stock in the hearth; (5) To a reduction in the volume of air forced into the furnace, and the resulting concentration of heat at the hearth; (6) Changes in the moisture content of the air. As a conse-

quence of the above changes, sometimes working in unison, and again at variance with each other, the production of cinder of constant composition is an unsolved problem. The writer has known one or two instances, when the cinder for two consecutive days showed exactly the same silica, but the laboratory was credited with this fine piece of metallurgical work. In the selection of samples, individual flushes are sometimes analyzed to represent the day's work, but the practice is bad, for the reasons given above, and it is preferable to sample each flush during the day of twenty-four hours. This is usually done by one of the furnace employees, by breaking equal sized pieces from the test mold samples taken during the day. These samples, properly labeled, are delivered at the laboratory early in the morning, and are there crushed in an iron or steel mortar by the boy to whom ths task is allotted, and the entire sample is passed through a 40 mesh sieve. In case the sample contains iron in the form of shot, these are thrown aside as not being part of the cinder. Only such iron should be shown in the analysis as is present in the form of oxide. Parts of the samples, sufficient for the analysis, are then placed in the agate mortar grinding machines, and are there ground till, in the judgment of the analyst, they are sufficiently fine, and the samples, after passing a magnet through them to separate any fine shot iron, are ready for the analysis.

Silica

In the determination of silica or, as it is commonly called, insoluble residue, on account of the method of analysis, 1 gram of the sample is weighed off into an 11 cm. porcelain dish, with a watch-glass cover; 10 cc. of water are added and the powder stirred up until it is all moistened. Ten cc. of strong hydrochloric acid are now added, and if the sample contains much iron a few drops of nitric acid. The solution, still covered, is evaporated to dryness over an Argand burner and thoroughly dried. When dry the dish is allowed to cool, and the residue is moistened with about 3 cc. of strong hydrochloric acid, and again evaporated to hard dryness. This is an essential point for rapid filtration, as a single evaporation, unless carried out in a platinum dish, does not dehydrate the silica, and this results in a loss of time in filtering. The dish is again allowed to cool, and the residue taken up with a mixture of 20 cc. of strong hydro-

chloric acid and 40 cc. of water, the large amount of hydrochloric acid being added to form ammonium chloride in the subsequent part of the operation. The dish and its contents are heated to near the boiling-point for a few minutes, and the solution filtered through a 9 cm. filter. Wash with hot water till free from chlorine, burn, and weigh. The native Bessemer ores used at present are practically free from barium, consequently volatilization of the silica with hydrofluoric acid is not needed.

The following are some comparative results by the above method, and those obtained by carbonate fusion, solution in water, acidifying with hydrochloric acid, evaporating to dryness, and treating as usual:

Insoluble residue by solution.		Silica by fusion.	
No.	Per cent.	No.	Per cent.
1	31.09	1	31.29
2	31.67	2	31.65
3	31.55	3	31.50
4	30.47	4	30.50
5	31.75	5	31.96
6	29.38	6	29.50
7	30.26	7	30.37
8	30.37	8	30.50
9	30.74	9	30.75
10	31.40	10	31.34

Iron and Alumina

Alumina.—The filtrate from the silica contained in a No. 3 beaker, with watch-glass cover, is heated to boiling, and a slight excess of strong ammonia added, and the solution boiled for a few minutes. The beaker is then removed from the heat and placed into a cold water-bath to cool and to cause the precipitate to settle. When the precipitate has settled completely, filter by decantation through an 11 cm. filter, keeping the paper full until the precipitate is reached. Then let the funnel drain and pour the precipitate on the filter with a steady stream until the beaker is drained. Wash with hot water until free from chlorine, burn, and weigh as iron and aluminum sesquioxides.

Iron.—Into a No. 2 beaker, without lip and with watch-glass cover, there had been previously weighed off 1 gram of the original sample; to this were added 30 cc. of water and 20 cc. of strong hydrochloric acid and the beaker set on the steam-bath to dissolve. This solution is now boiled for a few minutes till all

is dissolved, and the hydrogen sulphide all driven off. To this solution, while still hot, a slight excess of stannous chloride is added (about 3 drops), as the iron is all present in the ferrous form, and the solution diluted with cold water to about 300 cc. Ten cc. of the mercuric chloride solution are now added, the solution is stirred, and after waiting one minute, it is titrated with potassium bichromate solution, as previously described on page 37.[1] The iron is reported as iron, but subtracted as sesquioxide from the iron and alumina obtained before.

Lime

The filtrate from the alumina in a No. 4 beaker is heated to boiling and 25 cc. of a saturated solution of ammonium oxalate added, and 10 cc. of strong ammonia. This is boiled for a few minutes, removed from the heat, and the precipitate allowed to settle. It is then filtered through an 11 cm. filter, washed with hot water till free from chlorine, and burned in a muffle furnace, allowed to cool in a desiccator, and weighed as lime. The heat of a muffle furnace, at an ordinary red heat, will thoroughly decompose calcium oxalate, for in no case after treating as above, and then heating at the highest temperature of the blast-lamp, was there found a greater difference than 0.1 to 0.2 per cent. In case the cinder is high in magnesia, due to the use of all or part dolomite as a flux, a double precipitation is made of the lime as oxalate.

Magnesia

The filtrate from the lime, which need not exceed 400 or 500 cc., in a No. 5 beaker is cooled by placing it into a cold water-bath; it is then slightly acidulated with about 5 cc. hydrochloric acid, and for a cinder containing not over 8 per cent. of magnesia, 10 cc. are added of a 10 per cent. solution of sodium phosphate, and gradually from a measure, with constant stirring, 50 cc. of strong ammonia. Stir thoroughly and at intervals for two or three hours, then filter, wash with dilute ammonia (1 part ammonia, 3 parts water) till free from chlorine, burn, and weigh.

Manganese

The behavior of manganese in the furnace is similar to that of silicon. The higher the heat the more of the oxide is reduced

[1] *Proc. Eng. Soc. W. Pa.*, **11**, 253.

and alloys with the iron, and *per contra,* the lower the heat, the less is reduced, and the more remains in the cinder. In the method detailed above no attention has been paid to this element, part of the manganese being weighed with the oxide of iron and alumina, and part with the lime. The amount in the cinder is, as a rule, low, and the trifling error introduced, does not affect the metallurgical value of the results. Many determinations have been made by the writer of manganese in the iron and alumina and lime precipitates, as mentioned above, and in separate samples of the cinder, with the object of finding a rule whereby a certain amount of the total could be deducted from each, but without avail. And in case an accurate, complete analysis is desired, instead of ammonia precipitation of the iron and alumina, a double basic acetate precipitation must be made, and the manganese precipitated in the united filtrates with bromine, before precipitating the lime. Or to the cold filtrate from the silica sufficient bromine can be added to color the solution deeply and then a slight excess of ammonia (testing with litmus paper) and the solution boiled. The manganese is thus thrown down as oxide with the ferric oxide and alumina. A manganese determination by color in a separate portion of the sample and the metal calculated as Mn_3O_4, will give the amount to be subtracted from the iron oxide and alumina precipitate. For some time past the writer has been using the colorimetric method on cinders, exactly as it is used for the determination of manganese in pig iron and steel, with very satisfactory results.

Herewith are given some comparative results, using the colorimetric method and those obtained by the potassium chlorate method:

Colorimetric.		Potassium chlorate.	
No.	Per cent.	No.	Per cent.
1	0.40	1	0.42
2	0.41	2	0.40
3	0.31	3	0.29
4	0.35	4	0.33
5	0.47	5	0.48
6	0.23	6	0.22
7	0.27	7	0.26
8	0.30	8	0.31
9	0.33	9	0.32
10	0.36	10	0.36

Sulphur

A blast-furnace cinder will contain practically all the sulphur of the ore, flux, and fuel, less the amount contained in the iron, which amount is dependent on the temperature of the hearth. The higher the temperature the lower the sulphur, and *vice versa.* Cinders will vary in sulphur under normal conditions of ore and fuel, from 1 to 2 per cent., depending on the proportion of cinder produced to the ton of iron. The determination is effected as follows: Into a dry half-liter flask, introduce about one-half inch, equal to about 5 grams of chemically pure stick zinc, and then 0.25 gram of the cinder. The flask is provided with a doubly perforated rubber stopper; through one opening is placed a funnel tube, reaching to the bottom of the flask, and through the other a short piece of glass tubing, bent at right angles, and connected by a short piece of rubber tubing to the delivery tube, also bent at right angles, reaching to the bottom of a 1 in. by 10 in. test-tube, into which about 10 cc. of the ammoniacal solution of cadmium chloride are introduced, and the test-tube filled about three-fourths full of cold water. Ten cc. of water are now added to the flask, which is gently shaken till the cinder is moistened, to prevent caking on the bottom. The apparatus is connected, and 50 cc. of dilute hydrochloric acid added (1 part acid, 2 parts water). The cinder is dissolved almost instantly, liberating a large volume of hydrogen sulphide.

The compact zinc dissolves more slowly, liberatting hydrogen, which gradually displaces the hydrogen sulphide, and carries it over to the absorbent. A gentle heat is applied, which is gradually increased until the zinc is dissolved, and nothing but steam escapes from the delivery tube. The apparatus is then disconnected, and the solution titrated with iodine, using the same solution as is used for the determination of sulphur in iron or steel.

The following are some resuts obtained as above and compared with those obtained by fusion with the mixed carbonates and niter, solution, evaporation to dryness, solution, filtering, and precipitating with barium chloride.

Titrating with iodine. The evolved hydrogen sulphide. No.	Per cent.	Weighing as barium sulphate. No.	Per cent.
1	1.55	1	1.56
2	1.65	2	1.63
3	1.57	3	1.59
4	1.67	4	1.69
5	1.58	5	1.59
6	1.93	6	1.96
7	1.64	7	1.62
8	1.80	8	1.79
9	1.82	9	1.83
10	1.80	10	1.82

Phosphorus

Phosphorus, under normal conditions of temperature, is practically all reduced in the hearth of the furnace, and there combines with the iron, the amount remaining in the cinder varying from a trace up to 0.02 per cent., the average being much nearer the former than the latter figure. The determination is as follows:

Ten grams of the cinder are weighed off into a 12 cm. porcelain dish with watch-glass cover, and stirred up into a paste with water. Fifty cc. of strong hydrochloric acid are now added and 2 cc. of nitric acid, and the solution evaporated to hard dryness. The dish is allowed to cool and then moistened with about 25 cc. of strong hydrochloric acid, and again evaporated to hard dryness. When cool, from 15 to 20 cc. of strong hydrochloric acid are added, sufficient to moisten the residue, the dish and its contents are warmed for a few minutes, and warm water added to make up about 100 cc. Filter through an 11 cm. filter into a half-liter flask, and wash slightly with hot water. To the filtrate a slight excess of strong ammonia is added, about 25 cc., and then a slight excess of strong nitric acid, and the solution heated to 85° C., and 75 cc. of ammonium molybdate solution blown in by aid of a pipette. The flask is shaken for about five minutes, and the yellow precipitate collected and weighed the same as in ores, pig iron, or steel.

This analysis, like the determination of alkalies (which are ever present in cinders), has no known metallurgical significance, for they are beyond control, and it is but rarely if ever done, except for the gratification of idle curiosity, and in a furnace and steel works laboratory so much is wanted that is essential to the proper metallurgical operation of the plant, that scant time is left to curiosity.

The Analysis of Chrome and Tungsten Steels

By A. G. McKenna[1]

The writer has had occasion during the past few years to make complete analysis of several hundred samples of steel, containing both chromium and tungsten, and has found the following methods very satisfactory, accurate results being obtained without excessive care or unusual precautions.

The steel is usually too hard to be drilled, and is broken up in a steel mortar until no single piece is larger than a grain of rice. For the determination of sulphur, silicon, tungsten, manganese and chromium, 5 grams are weighed into a 500 cc. evolution flask, so arranged that the gases evolved on the addition of 30 cc. hot water, and 30 cc. concentrated hydrochloric acid shall be absorbed by an ammoniacal cadmium chloride solution contained in a large test-tube. The solution is made as rapidly as possible by the application of heat; as there seems to be evidence that with some irons lower results are obtained by the evolution method when cold acid is used. When the steel has dissolved the solution is boiled for a minute or two until no more hydrogen remains in the flask, it being displaced by steam. The sulphur is then determined by titration with iodine in the usual manner, using starch solution as an indicator. By adding a few grams of zinc chloride to the starch solution it can be kept indefinitely without spoiling. The solution in the evolution flask is transferred to a 500 cc. Erlenmeyer flask. Ten cc. of strong nitric acid are added and the solution evaporated to dryness on a hot plate, taken up with 15 cc. strong hydrochloric acid, evaporated again to dryness, taken up with 20 cc. strong hydrochloric acid, diluted with hot water to about 100 cc., boiled, and filtered. All the silica and tungstic acid will be on the filter-paper; after washing thoroughly with a 5 per cent. nitric acid solution the residue is ignited in a weighed platinum crucible as $WO_3 + SiO_2$ and weighed. A few drops of hydrofluoric acid are now added and the crucible is heated to a bright red for five minutes to volatilize silica. The loss is silica which is

[1] *Proc. Eng. Soc. W. Pa.*, **16**, 119.

calculated to silicon; the residue in the crucible is tungstic acid, which is calculated to tungsten. This residue generally contains a trace of iron oxide which can be easily determined by fusing the residue, after the weight has been taken, with sodium carbonate, and filtering off the oxide of iron after solution in hot water.

The filtrate from the tungstic acid and silica is again transferred to an Erlenmeyer flask and evaporated to a small bulk. Fifty cc. of concentrated nitric acid are now added and the solution boiled until no more fumes come off, showing that all hydrochloric acid has been removed. Enough concentrated nitric acid is added to make the volume 200 cc., and the solution again heated. When it has reached the boiling-point, 10 grams of potassium chlorate are added and the solution boiled down to 75 cc. in order to remove all chlorine.

The manganese will now be completely precipitated as manganese dioxide and the chromium will be converted to chromic acid.

The solution is filtered on an asbestos plug while hot, which is washed a few times with freshly boiled concentrated nitric acid. In the filtrate, chromium is determined by titration with ferrous sulphate and permanganate according to the following reactions:

$$2CrO_3 + 6FeO = 3Fe_2O_3 + Cr_2O_3.$$

$$2KMnO_4 + 10FeO = K_2O + 2MnO + 5Fe_2O_3.$$

If the solution is diluted to about 500 cc. and cooled to about 20° C., before titration, there is not the slightest danger of interference by the nitric acid. The manganese dioxide on the asbestos plug is dissolved by hot hydrochloric acid and a pinch of potassium nitrite. It is brought to a boil to drive off chlorine and the traces of iron are precipitated by ammonia and ammonium acetate; the basic precipitate is dissolved and reprecipitated to free from traces of manganese. In the filtrate manganese is precipitated by bromine in a strongly ammoniacal solution, filtered, ignited and weighed as Mn_3O_4.

For the determination of phosphorus, 5 grams are weighed into a porcelain dish and 60 cc. of dilute nitric acid added. If the steel contains more than 1 per cent. of chromium it will probably be found necessary to add hydrochoric acid from time to time to secure solution. Solution must be complete before allowing the evaporation to go too far, or it will be found almost impossible to dissolve the last particles of steel.

The residue is baked as usual in phosphorus determinations, 20 cc. hydrochloric acid are added and the solution again taken to dryness, taken up in 20 cc. hydrochloric acid, again diluted and filtered from tungsten and silicon, which may be ignited and weighed as a check on the first determination. To the hydrochloric acid solution, 35 cc. strong ammonia are added, then sufficient strong nitric acid to redissolve the iron hydroxide. 100 cc. molybdate solution, made according to Wood's formula as given by Blair, are added to the flask, which is then shaken for a few minutes to insure complete precipitation of the phosphorus. After standing for an hour the yellow precipitate is filtered through a dried weighed paper, washed with dilute 1 per cent. nitric acid, dried for an hour and weighed as phosphomolybdate, containing 1.63 per cent. phosphorus.

For carbon, 1.5 grams are dissolved in 100 cc. of a 33 per cent. copper and potassium chloride solution. After standing half an hour 5 cc. hydrochloric acid are added to hasten solution. When all the precipitated copper has redissolved, the solution is filtered through ignited asbestos in a platinum filter tube, using suction to hasten filtration. The carbon on the plug is washed a few times with hot water, then dried and burnt in a platinum tube with a stream of oxygen. The CO_2 is absorbed as $BaCO_3$ in a barium hydroxide solution contained in a 10-bulb absorption tube, filtered, washed well with freshly boiled distilled water, ignited, and weighed as $BaCO_3$, containing 6.09 per cent. carbon.

A Quick Method for the Determination of Carbon in Ferrochrome

By A. G. McKenna

Mix thoroughy 0.2 gram finely ground ferrochrome with 1.5 gram sodium peroxide. Place the mixture into a small narrow copper crucible and fuse by placing the crucible upon a piece of iron previously heated to redness. The reaction is rapidly completed and all the carbon remains as sodium carbonate. From this sodium carbonate the carbon dioxide is expelled by decomposition with an acid. The carbon dioxide is received in a solution of barium hydroxide. The barium carbonate produced is filtered, ignited, and weighed in a platinum crucible.

The Complete Analysis of Chrome Ore

By A. G. McKenna

A serious objection to most methods of chrome ore analysis has been the difficulty of obtaining complete decomposition of the ore without prolonged and repeated fusions with the reagents generally employed for that purpose. By fusing the ore with sodium peroxide, chrome ore is completely decomposed in a few minutes. The fusion should not be made in platinum as the peroxide attacks the crucible strongly. A nickel crucible is the best for the purpose, although it also is attacked and cannot be used more than twenty or thirty times. On leaching out the fusion with water all the chromium goes into solution as sodium chromate; the oxides of iron, nickel, and magnesium remain in the undissolved residue. The following method for the determination of silica, oxides of chromium and iron, alumina, lime, and magnesia, is based on the above-mentioned facts.

Determination of Bases and of Silica

One-half gram of the finely ground sample, which has been dried at 100° C. for one hour, is weighed into a nickel crucible of about 20 cc. capacity, in which have been placed 3 or 4 grams of sodium peroxide. After thoroughly mixing the contents, the crucible is held over a Bunsen burner by means of a suitably shaped tongs until fusion begins. The mass is kept in a liquid condition at a low red heat for about one minute which is sufficient to insure complete decomposition if the ore is at all finely ground. After allowing the crucible to cool it is placed into a 400 cc. beaker with a watch-glass cover, and hot water added until the crucible is covered. The beaker is placed on a hot plate until the fusion is dissolved; the crucible is then removed by means of a glass rod, and the contents of the beaker allowed to settle for a few minutes. When the insoluble matter has subsided it is collected on a 9 cm. filter, the filtrate being received in

a half-liter flask. The residue on the filter which contains all the iron is dissolved in dilute sulphuric acid (1:10), reduced by filtration through amalgamated zinc, and titrated in the usual manner with standard permanganate solution. The result is calculated to ferrous oxide.

The filtrate in the half-liter flask, which contains all the chromium as sodium chromate in alkaline solution, is boiled for about ten minutes in order to insure the decomposition of all peroxide which, if allowed to remain until the solution is acidified, would react on the chromate, reducing it to the sesquioxide. When the decomposition of the peroxide is complete the solution is allowed to cool, and then acidified with a large excess of dilute sulphuric acid (1:4). The solution is transferred to a liter beaker and diluted to about 800 cc. with cold water. To this solution 100 cc. of a ferrous sulphate solution containing 7 grams of iron as ferrous sulphate in 1 liter are added. This is sufficient to reduce the chromic acid corresponding to 0.3167 gram of chromium sesquioxide. The excess of ferrous sulphate, which has been added, is determined by titration with standard permanganate solution, of which 1 cc. is equivalent to 1 cc. of the ferrous sulphate solution. Such a permanganate solution contains 5.643 grams of potassium permanganate in 1 liter. The difference between the number of cubic centimeters of ferrous sulphate, and of permanganate used, multiplied by 0.905, gives the percentage of chromium sesquioxide in the ore.

For the determination of silica fuse 0.5 gram of the ore in a nickel crucible as before, dissolve in about 50 cc. hot water in a covered 12 cm. porcelain dish, remove the crucible, and acidify with hydrochloric acid, evaporate to dryness, take up with dilute hydrochloric acid, evaporate to dryness, take up with dilute hydrochloric acid (1:4), filter, ignite, and weigh as SiO_2.

To determine the aluminum, chromium, calcium, and magnesium, fuse 0.5 gram with sodium peroxide in a nickel crucible as before, dissolve out in hot water, boil, and filter. All the ferric oxide, magnesia, lime, and nickel oxide (which latter is derived from the crucible) remain on the filter. In the filtrate the alumina and most of the silica are found. Dissolve the residue on the filter in hydrochloric acid, precipitate twice with ammonia, and separate lime and magnesia in the usual way by ammonium oxalate, and precipitate the magnesia by ammonium

phosphate. The nickel remains in solution and does not interfere. To the alkaline filtrate from the insoluble residue add hydrochloric acid and evaporate to dryness, take up with hydrochloric acid, dilute, filter to remove the silica, and precipitate with ammonia for the determination of the alumina.

The Analysis of Slags

By A. B. Harrison

Weigh out 0.25 gram of the sample and suspend in 30 cc. of water, in a 10 cm. evaporating dish. Dissolve in 30 cc. of dilute hydrochloric acid, cover with a watch-glass and evaporate to dryness over a small flame or on a hot-plate. Cool, take up with 30 cc. of dilute hydrochloric acid, boil till all salts are in solution, and filter through a quick filter-paper. Wash the precipitate, using hot water, burn in a platinum crucible, cool, and weigh as silicious residue. Usually there is no need of fusing this residue, and it can be reported as silica. In case barium salts or titanium is suspected, the residue should be fused with sodium carbonate and the silica freed from these impurities.

Determination of Alumina and Ferric Oxide

To the filtrate from the silicious residue add a few drops of nitric acid, boil and add a slight excess of dilute ammonia. Boil till the liquid no longer smells of ammonia, filter through a No. 2 12.5 cm. Swedish paper, wash with hot water, burn, and weigh as Al_2O_3 and Fe_2O_3. The filtrate and washings should be caught in a 500 cc. Griffin beaker.

Determination of Lime

The filtrate from the alumina and ferric oxide precipitate is brought to boiling, and, while boiling, 50 cc. of hot ammonium oxalate solution are added. Boil for two or three minutes, allow to settle, filter through a 12.5 cm. No. 597 S and S paper, washing the precipitate with hot water till free from oxalate. Then remove from the funnel and, without disturbing the filter-paper, wash out as much of the precipitate as possible with the wash-bottle into the beaker in which the precipitation was made. Then carefully unfold the paper and, allowing it to rest against the side of the beaker, wash off all adhering particles into the beaker. Add 100 cc. of dilute sulphuric acid and bring to boiling; while boiling, titrate with potassium permanganate soution. The

number of cubic centimeters of permanganate solution used, multiplied by the factor, gives the percentage of lime in the sample.

The factor is obtained by multiplying the iron value by 2 (this applies in case of a 0.25 gram sample).

Determination of Magnesia

The filtrate from the lime precipitate is concentrated in an 800 cc. Griffin beaker to about 250 cc. and cooled. When cool, add a slight excess of ammonia, and stir in microcosmic salt solution, and 20 cc. of ammonia (sp. gr. 0.96). Stir for a minute or two, and allow to stand in cold water for six hours; filter through an ashless paper, wash with 20 per cent. ammonia, burn, and weigh as $Mg_2P_2O_7$, containing 0.36 part magensia.

Note.—When the silicious residue has been fused, determine in the filtrate from the silica, the barium as barium sulphate, and the titanium as directed by Blair ("Chemical Analysis of Iron," third edition); also determine the small amounts of alumina and ferric oxide, which add to the amount found in the original filtrate. It is very seldom that lime or magnesia will be found in the residue, but determine any if present, adding the amounts to that found in the original solution of the sample. The silicious residue may be treated with hydrofluoric acid and sulphuric acid and the silica found by difference.

The alumina may also be determined directly by using the method of J. M. Camp, on page 143.

Determination of Sulphur

Method by Oxidation with Aqua Regia.—Weigh out 1 gram into a 10 cm. evaporating dish and add water. Add a drop or two of bromine and dissolve in 50 cc. of freshly made aqua regia. Evaporate to dryness with the usual precautions. Proceed as in the determination of sulphur in ores.

Evolution Method.—The method described by J. M. Camp on page 41 is used.

Determination of Manganese

The various standard methods are used. The color method gives good results if carefully carried out.

Determination of Iron

Weigh out 5 grams of the sample into a 10 cm. evaporating

dish and suspend in 30 cc. of water. Dissolve in 30 cc. of dilute hydrochloric acid, cover with a watch-glass, and evaporate to dryness. Cool and take up with dilute hydrochloric acid, boil till all iron is in solution, filter, and wash by decantation, using water and dilute hydrochloric acid, till the residue in the dish is free from iron; wash free from iron and determine iron by titration with potassium bichromate, as given in the analysis of iron ores. Calculate the iron to ferric oxide and subtract from the amount found under alumina. The difference is reported as alumina.

The Analysis of Mill Cinder

By A. B. Harrison

Determination of Phosphorus

Weigh out 2 grams of flue cinder, or 1 gram of tap cinder, into a 10 cm. round-bottomed evaporating dish; suspend in 50 cc. of water, and add 50 cc. of concentrated hydrochloric acid. Cover with a watch-glass and evaporate to dryness; bake, and cool. Take up with dilute hydrochloric acid and boil until all iron is in solution; filter through a Swedish paper, decanting as much of the liquid as possible; wash the residue with water, and finally transfer the residue to the filter. Wash the paper and residue free from iron, etc., using hot dilute hydrochloric acid and water alternately. Burn and weigh as silicious residue. Fuse this residue with sodium carbonate and separate the silica in the usual manner. Combine the filtrates and proceed for the determination of the phosphorus as in the analysis of pig iron.

Determination of Silica

Weigh out 0.5 gram of the sample and suspend it in water, dissolve in 50 cc. of strong hydrochloric acid, evaporate to dryness, and bake. Cool, moisten with strong hydrochloric acid, and again evaporate and bake. Take up with 50 cc. dilute hydrochloric acid, boil till all iron is in solution, filter, wash free from iron, burn, and weigh the silicious residue. Fuse with sodium carbonate and dissolve the fusion in the usual manner. Evaporate the solution of the fusion to dryness and bake. Take up with dilute hydrochloric acid, and filter off the silica, receiving the filtrate and washings in the beaker containing the first filtrate. Burn, and weigh as SiO_2.

Concentrate the combined filtrates to 100 cc., add a drop or two of nitric acid, boil, and add a slight excess of ammonia; boil till the solution no longer smells of ammonia, filter, dissolve in dilute hydrochloric acid, and reprecipitate. Filter, receiving the filtrate and washings into the beaker containing the first filtrate. Burn, and weigh as oxides of iron, aluminum and phosphorus. From

this weight subtract the sum of the weights of ferric oxide and phosphorus pentoxide, and calculate from the difference the percentage of alumina.

Alumina is also determined as phosphate by the method described by J. M. Camp, page 143.

Determination of Lime

To the filtrate from the ammonia precipitate, after concentration, add 10 cc. of ammonium oxalate solution. Boil for a few minutes, and allow to settle. Filter through a small ashless paper; wash with hot water, burn, and weigh as CaO.

Determination of Magnesia

Concentrate the filtrate and washings from the lime precipitate to 250 cc., cool and add 10 cc. of microcosmic salt solution, stirring briskly and adding the precipitant slowly. Then add 30 to 50 cc. of ammonia (sp. gr. 0.96). Stir for a minute or two and allow to stand in ice-water for from two to six hours. Filter through a small ashless paper and wash with a ten per cent. ammonia wash-water. Burn and weigh as magnesium pyrophosphate, containing 0.36 part of magnesium oxide.

Determination of Manganese

Volhard's method and also Ford-Williams' method are used.

Determination of Iron

See the method described for iron in iron ores.

Determination of Sulphur

See the method described for sulphur in iron ores.

In analyzing materials high in silica, such as mill cinders, slags, or cements, always suspend in water before adding acid. This will help to prevent "caking."

In phosphorus determinations in cinder from steel, weigh out 5 grams. Also make a basic acetate separation when determining alumina, lime, etc., unless the cinder contains a small amount of manganese, in which case proceed as above.

A Rapid Method for Phosphorus Determination in Iron and Steel[1]

By James O. Handy

Principle: One molecule of ammonium phosphomolybdate requires 23 molecules of sodium hydroxide (or equivalent alkali), for its neutralization.

$$2[(NH_4)_3 12MoO_3PO_4] + 46NaOH + H_2O =$$
$$2[(NH_4)_2HPO_4] + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23H_2O.$$

In practice the phosphomolybdate obtained free from adherent acid by the necessary washing, is dissolved without heat in an excess of standard sodium hydroxide solution, and, after addition of phenolphthalein, the excess of alkali is titrated with standard acid. The acid and alkali are equivalent and are of such strength that 1 cc. = 0.0002 gram of phosphorus, or 0.01 per cent. when 2 grams of metal have been used for analysis.

The method for steels containing less than 0.75 per cent. carbon, and for pig iron low in combined carbon is given below. Higher carbon steels, ferromanganese, and pig irons are dissolved in nitric acid (sp. gr. 1.13), the solution evaporated to hard dryness, the residue treated with hydrochloric acid, boiled, diluted, and filtered, then made ammoniacal, and afterward thoroughly acid with nitric acid, heated to 85° C., and precipitated with ammonium molybdate solution.

If the analysis of metal known or suspected to contain arsenic, precipitate at 75° C., filter, and wash as usual. Dissolve the precipitate in 15 cc. of ammonium hydroxide (1:6), dilute the solution to 75 cc., heat to 75° C., and add a mixture of 10 cc. nitric acid (sp. gr. 1.42), and 25 to 50 cc. of molybdate solution (Wood's formula). Shake well, filter, and wash. The precipitate is now free from arsenic and may be further treated in the usual way.

The Method

Dissolve 2 grams of steel contained in a 12 oz., Erlenmeyer

[1] *Proc. Eng. Soc. W. Pa.*, **8**, 78.

flask, in 75 cc. of nitric acid (sp. gr. 1.13). To the boiling solution, free from red fumes, add 15 cc. of 0.5 per cent. potassium permanganate solution. Continue boiling until the pink color disappears. If no precipitate of brown oxide of manganese remains, add more potassium permanganate. When a permanent brown precipitate remains place the flask on a cool, dry piece of asbestos-paper and add gradually about 50 mg. of pure granulated sugar. Boil the solution until clear. Remove the flask from the plate and, after two or three minutes, add 13 cc. of ammonia water (sp. gr. 0.90). If the flask is held at an angle of 45° no loss by spattering need occur. Shake until the ferric hydroxide redissolves. Heat or cool to 85° C., add 50 cc. of molybdate solution, stopper, insulate by wrapping, and shake for five minutes, mechanically or by hand. Filter immediately through a 9 cm. No. 0 filter-paper, using suction if necessary. Wash the flask and filter thoroughy with 1 per cent. nitric acid, then with 0.1 per cent. potassium nitrate solution, or with water alone until all acid is removed.

Place the filter and contents into the flask. Add from a pipette 10 cc. at a time of the standard sodium hydroxide solution until, on stirring, the yellow precipitate all dissolves. Dilute with water to about 50 cc. Add from 3 drops to 0.5 cc. of 1 per cent. alcoholic solution of phenolphthalein, and titrate to the disappearance of the pink color. The number of cubic centimeters of standard sodium hydroxide solution, neutralized by the phosphomolybdate, represents hundredths per cent. of phosphorus in the sample analyzed.

SOLUTIONS

Molybdate Solution, Wood's formula.—One pound of molybdic acid is mixed with 1.2 liters of water in a stoneware jar; 700 cc. of ammonia water (sp. gr. 0.90) are stirred in, and agitation continued until all soluble matter is dissolved.

300 cc. of nitric acid (sp. gr. 1.42) are added to partially neutralize the ammonia. Place into each of four 2.5 liter bottles a mixture of 500 cc. nitric acid (sp. gr. 1.42) and 1200 cc. of water.

Pour 550 cc. of the molybdic acid solution through a funnel into each bottle and mix by a slight rotating movement. If the stream flows quickly and continuously, no separation of molybdic acid occurs. Allow to stand several hours and filter before use.

Standard Sodium Hydroxide Solution.—One cc. = 0.0002 gram of phosphorus. A solution of sodium hydroxide of 1.5 decinormal strength closely approximates to the value required. It is best made as follows: 100 grams of a good grade of caustic soda are stirred thoroughly with water not quite sufficient to dissolve. The solution, when saturated, is poured into a dry glass cylinder, about 30 × 2.5 cm., stoppered, and allowed to clarify. The sodium carbonate settles, usually in a few hours, leaving a saturated solution of sodium hydroxide free from carbonate. 26 + cc. of this solution will make about 2 liters of standard sodium hydroxide solution. Place 20 cc. into a 1 liter graduated cylinder, make up to 1 liter, and mix. Titrate against the standard acid and dilute as much as is required to make the solutions equivalent. Base the final standardization on a steel of known phosphorus content.

Standard Nitric Acid.—One cc. = 0.0002 gram phosphorus. Twenty cc. of nitric acid (sp. gr. 1.42) are diluted to 1 liter in a graduated cylinder. Titrate with standard sodium hydroxide solution. Dilute until equivalent to the alkali.

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